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PROGRESS IN
INORGANIC CHEMISTRY

Volume 1

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PROGRESS IN
INORGANIC CHEMISTRY

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VOLUME 1

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Introduction to the Series

The remarkably broad and rapid development of inorganic chemistry since the end of World War II is well recognized. If we chose to define inorganic chemistry as the study of all of the chemical and many related physical properties of inorganic substances, the extent of the field is very great indeed. It includes among its ramifications the organo derivatives of all of the elements, the study of mixed oxide systems, the quantum mechanical treatment of the spectral and magnetic properties of transition metal ions, the study of a wide variety of catalytically active solids, the preparation of a host of the less familiar elements and their compounds, as well as radically new types of compounds, along with the many classically recognized aspects of inorganic chemistry. The wide interest and the rapid growth and expansion of the field are attested by the great and persistent demand for inorganic chemists for both industrial and academic positions. The new Division of Inorganic Chemistry of the American Chemical Society, which received permanent status recently, symbolizes the general recognition of inorganic chemistry as a distinct and plenary branch of the science.

Because of the breadth and diversity of the discipline, the problem of maintaining effective, fruitful communication among the different branches of inorganic chemistry has become highly important. It is my belief that a new forum for the exchange of views and for critical and authoritative review and evaluation of advances in the various branches of the discipline would be of great value. The annual series of volumes of which this is the first has been initiated with the hope that it will contribute to meeting the need for communication.

It is intended that all articles be written by one of the leading researchers in the field. The treatment is intended to be such that the article should be comprehensible, but not necessarily *readily* comprehensible, to a competent Ph.D. level research worker in some branch of inorganic chemistry, but not necessarily the one under discussion. However, it is my belief that the author's responsibility and privilege of giving a scholarly and accurate account of his subject should not be curtailed by any feeling of a need for oversimplification. If, for example, a subject is intrinsically complicated or mathematical, no useful purpose can be served by dealing with it as if it were not. Thus I have hoped to include articles which avoid both of the extremes, first, of dry and terse summarizing of the literature and, second, of superficiality suitable perhaps for light reading but not very helpful to the reader desiring accurate, thorough information. I have encouraged a degree of informality so that where responsible differences of opinion exist the expression of the author's own viewpoint, consistent with fairness and decorum, may be presented. Length and style will also be found to vary from one article to another, since I have assumed that the author is best qualified to determine the style, length, and general nature of the treatment appropriate to his subject.

It is also my hope that these volumes will be regarded as, and become progressively more of, an international venture, which is in the true spirit of science. With this in mind, articles will be published in any of the three languages, English, German and French, which research chemists are assumed to read.

I should greatly welcome comments and suggestions with regard to any aspect of these volumes.

In conclusion, it is my duty to emphasize that it is the authors of the articles who are responsible for their excellence and it is my pleasure to express my gratitude for their efforts.

F. A. Cotton

Cambridge, Mass.
June 25, 1959

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Cyclopentadienyl and Arene Metal Compounds

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I. Introduction

A. SCOPE

This review covers the chemistry of compounds formed between transitional metals and the cyclopentadienyl group, benzene and related aromatic systems, and certain other unsaturated hydrocarbons. It deals also with the ionic derivatives of the cyclopentadienide ion and with the cyclopentadienyl derivatives of certain nontransition metals.

While the first metal derivatives of cyclopentadiene were prepared by Thiele over fifty years ago, the interest in metal derivatives of cyclopentadiene, and subsequently of aromatic hydrocarbons, stems from the independent and accidental discoveries of the molecule of formula $C_{10}H_{10}Fe$, now called ferrocene, by Miller, Tebboth, and Tremaine (B.9) and by Kealy and Pauson (B.1).* These authors did not fully appreciate the unique nature of the compound either structurally or in its chemical behavior, and shortly thereafter the now well-known "sandwich"* structure was advanced by Wilkinson, Rosenblum, Whiting, and Woodward (B.2) and later, independently, by Fischer and Pfab (B.10). It was also shown by Rosenblum, Whiting, and Woodward (O.0) that the molecule behaves as an aromatic system undergoing, for example, Friedel-Crafts acylations; they also coined the name "ferrocene" for $(\pi\text{-}C_5H_5)_2Fe$.

---

* Ferrocene was first obtained in 1948 during studies of possible reactions of olefins with nitrogen over metallic catalysts in the laboratories of the British Oxygen Company (S. A. Miller, private communication to G. W.).

The early studies in the field were comprehensively reviewed in 1955 (E.20) and other reviews of parts of the field have been made (E.2,F.33,F.34,G.25,H.16,H.34,H.35). The present review is concerned primarily with the general inorganic and physical chemistry of the compounds and with theoretical treatments of bonding. The now exceedingly extensive organic chemistry of ferrocene is not discussed, although a literature guide is provided. The references are believed to be complete up to July 1, 1958.

Excluding various salts, e.g., picrates, Reineckates, etc., of cations such as $(\pi\text{-}C_5H_5)_2Co^+$ and $(C_6H_6)_2Cr^+$ and organic derivatives of ferrocene, the tables presented subsequently indicate that since the discovery of ferrocene in all over 200 new metal-hydrocarbon compounds have been prepared. It is pertinent to note, however, that while many of the cyclopentadienyl and arene compounds discussed herein have been described by different workers, often quite simultaneously, in the scientific literature, it is known that many of these derivatives were made and studied at least simultaneously and in quite a few cases earlier in industrial laboratories. It is not possible to give these often unknown industrial investigators due credit except in occasional patent references, where detailed studies are seldom given. Thus it appears that $(\pi\text{-}C_5H_5)_2Ni$ was first made by Thomas (P.3) and several carbonyl derivatives, e.g., $\pi\text{-}C_5H_5M(CO)_3H$ (M = Cr, Mo, W), appear to have been made first in industry (P.21,P.21a). Attention may be drawn at this point to the remarkable patent (P.21,P.21a), which would appear from its date of filing to anticipate much published work not only on carbonyl compounds but on preparative methods for di-π-cyclopentadienyl compounds and cyclopentadienides. The patent is remarkable in other ways, too, indeed having semblance in parts to science fiction; thus even those "skilled in the art" would have some difficulty in isolating compounds mentioned in the claim, such as $(C_5H_5)_5La(PBr_3)_2$ or $(C_5H_5)Li(H_2O)$, and in proving that "$(C_5H_5)Ti(NO)_3$ is more stable than $(C_5H_5)V(NO)_2H_2$."

---

* The first users of this term were Dunitz and Orgel (C.6).

It may be noted, finally, that since the discovery of ferrocene, we have listed over 300 notes and papers on the sandwich compounds reviewed herein.

B. NOMENCLATURE

The nomenclature adopted is as follows:

1. *Cyclopentadienyl Compounds*

(a) Two rings present with "sandwich" bonding: di-π-cyclopentadienyl-, e.g., di-π-cyclopentadienylchromium(II), $(\pi\text{-}C_5H_5)_2Cr$. The name *ferrocene* is used for $(\pi\text{-}C_5H_5)_2Fe$; the cation $[(\pi\text{-}C_5H_5)_2Fe]^+$ is termed the ferricenium ion. Similar trivial names are ruthenocene, osmocene, cobaltocene, nickelocene, etc.

(b) One ring present with "sandwich" bonding: π-cyclopentadienyl-, e.g., π-cyclopentadienylchromium(II) dinitrosyl chloride, $\pi\text{-}C_5H_5Cr(NO)_2Cl$.

(c) One or two rings present with localized metal–carbon bonds: σ-cyclopentadienyl-, e.g., π-cyclopentadienyl(σ-cyclopentadienyl)-chromium(II) dinitrosyl, $\pi\text{-}C_5H_5Cr(NO)_2\sigma\text{-}C_5H_5$.

(d) Ionic derivatives: cyclopentadienide ion, $C_5H_5^-$; cyclopentadienides, e.g., manganese cyclopentadienide, $Mn(C_5H_5)_2$.

2. *Arene Compounds*

(a) Two rings present: diarene-, e.g., dibenzenechromium(0), $(C_6H_6)_2Cr$.

(b) One ring present: arene-, e.g., toluenechromium(0) tricarbonyl, $C_7H_8Cr(CO)_3$. A similar nomenclature is used for other aromatic or pseudoaromatic systems, e.g., cycloheptatrienechromium(0) tricarbonyl, $C_7H_8Cr(CO)_3$.

3. Abbreviations

π-Cp = π-C_5H_5
σ-Cp = σ-C_5H_5
Cp^- = $C_5H_5^-$
π-ind = π-indenyl
σ-ind = σ-indenyl
σ-fluor = σ-fluorenyl
m.p.d. = melting point with decomposition

d. = decomposes without melting
MeCp = methylcyclopentadiene
Me = methyl
Et = ethyl
bz = benzene
tol = toluene
mes = mesitylene
ϕ = phenyl

II. Cyclopentadienides

A. GENERAL REMARKS

It is pertinent to include in this review some brief notes on the ionic derivatives of cyclopentadiene—the cyclopentadienides— since not only are the alkali metal and magnesium salts used in preparations of other metal derivatives, but the manganese compound of formula $C_{10}H_{10}Mn$ has been shown to be a cyclopentadienide unlike the other $(\pi\text{-}C_5H_5)_2M$ compounds of the elements of the first transitional series.

The acidity of cyclopentadiene was first recognized by Thiele, who obtained the potassium salt (A.3,A.4) as an air-sensitive product by treating dispersed potassium in benzene with C_5H_6 at room temperature; he obtained no reaction with sodium (A.4). Thiele's discovery led to similar work with substituted cyclopentadienes, and the potassium salt from fluorene was first made (A.5) by melting fluorene with KOH at 250–280°C. Sodium indenylide was obtained somewhat later (A.6) by the reaction of sodium with indene in the presence of ammonia or organic bases; sodium and lithium derivatives were subsequently made of indene, fluorene, and their derivatives.

The Grignard reagent, $MgBrC_5H_5$, and the corresponding indene derivative have long been known and used preparatively (A.1,A.2, A.7). These are obtained by treating an alkyl Grignard reagent in ether, or preferably in a higher boiling solvent such as benzene, with the hydrocarbon. The fluorene derivative was similarly obtained.

Concerning the cyclopentadienides, little further work was done for many years, until Greenlea (A.8) showed that in liquid ammonia solution cyclopentadiene reacted rapidly with sodium, without evolution of hydrogen, according to reaction 1. He isolated cyclo-

$$2\,Na + 3\,C_5H_6 = C_5H_8 + 2\,NaC_5H_5 \qquad (1)$$

pentenes in yields consistent with this stoichiometry. This work anticipated by fourteen years similar studies using liquid ammonia (F.4,F.5) in which the same conclusions were drawn concerning the stoichiometry of the sodium reaction and the formation of cyclopentenes; both the later groups noted that the stoichiometry of the reaction given by Fischer *et al.* (C.7–C.10) requiring the evolution of hydrogen is false. The properties of sodium cyclopentadienide and the preparation of the calcium salt, either by reaction of cyclopentadiene with calcium carbide at elevated temperatures or by reaction in liquid ammonia, were also given by Ziegler *et al.* (D.1,F.5).

The formation of solutions of sodium cyclopentadienide in ether solvents (D.3,F.23) is now widely used for preparative work and is perhaps the most generally useful method for preparing all types of nonionic cyclopentadienyl metal compounds and indeed even sublimable cyclopentadienides such as those of manganese and the lanthanides. The use of the sodium salt is more expeditious than methods requiring the use of lithium cyclopentadienide or the Grignard reagent. Suitable ethers for carrying out the reaction of granular or dispersed sodium with cyclopentadiene (or substituted cyclopentadienes) are tetrahydrofuran, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, etc., of which the first two are most commonly employed. Sodium may be dispersed in mineral oil, to which the ether is then added (P.21) or may be granulated in toluene which is then removed and the ether run in (F.23). Details for a laboratory preparation have been given (F.32).

It has been shown (D.8) that potassium tertiary butoxide converts cyclopentadiene quantitatively to its potassium salt; this fact, together with the fact that indene and fluorene do not react with the sodium tertiary butoxide (F.5), confirms estimates (D.8 and references therein) that the pK_a value for cyclopentadiene is greater than 19 and less than the 21 of indene. The formation of sodium, potassium, and lithium cyclopentadienides in alcohols and in other solvents of high dielectric constant is possible, e.g., lithium cyclopentadienide has been made in dimethylformamide (F.39,F.44), and calcium cyclopentadienide has been made in ethylenediamine (F.5). The sodium salt has also been made in inert solvents containing a small amount of alcohol (F.5).

Equations 2 and 3 illustrate the general behavior of cyclopentadienides. Thus, in tetrahydrofuran, rather weakly conducting solu-

$$M^+C_5H_5^- = M^+ + C_5H_5^- \tag{2}$$

$$C_5H_5^- + H^+ = C_5H_6 \tag{3}$$

tions of NaC_5H_5, $Mn(C_5H_5)_2$, and $Mg(C_5H_5)_2$ were obtained (F.23), indicating that while dissociation does occur, it is not, however, substantial. With acids which are stronger than cyclopentadiene, e.g., water, cyclopentadienides react instantaneously to form cyclopentadiene and the metal hydroxide or other salt. The cyclopentadienides generally react vigorously with air, inflaming or smoldering in the solid state. They also react with carbon dioxide to give carboxylic acid salts (A.4) and with dienophiles such as maleic anhydride; with chloroform and with alkyl halides they give alkylated cyclopentadienes.

The dissociation is also shown by the fact that all cyclopentadienides react instantaneously in an ionic reaction, and quantitatively* with ferrous chloride (or other metal halides) to give ferrocene (eq. 4). The criteria for ionic bonding in metal cyclopentadienyl compounds based on both physical measurements and chemical reactions such as those above have been discussed at some length in studies of manganese cyclopentadienide (F.23).

$$2\,C_5H_5^- + Fe^{2+} = (\pi\text{-}C_5H_5)_2Fe \tag{4}$$

The high resolution nuclear magnetic resonance chemical shift of the equivalent protons of the $C_5H_5^-$ ion has been measured and compared to the shifts for protons in benzene and the tropylium ion $C_7H_7^+$ (G.39). The Pople free electron theory of shifts in aromatic rings predicts that the resonance in the $C_5H_5^-$ ion should be upfield, and that in $C_7H_7^+$ downfield, from that in benzene. Qualitatively, these predictions are confirmed, but quantitatively the agreement is rather poor, the observed shifts being much larger than those calculated. The differences may perhaps be accounted for by the reasonable assumption that part of the negative charge in the $C_5H_5^-$ ion spreads to the hydrogen atoms, thus putting them further upfield, while the opposite occurs in the $C_7H_7^+$ ion.

---

* While the reaction of pure cyclopentadienides, e.g. $Mn(C_5H_5)_2$ and $Pr(C_5H_5)_3$, was shown to be quantitative with Fe^{2+}, the reaction of NaC_5H_5, prepared in ether from C_5H_6 and Na, does not give quantitative yields of ferrocene, presumably since some reduction to cyclopentenes occurs. Although not quantitatively studied, this reduction appears to be much less in the ethers than in liquid ammonia; hydrogen is certainly evolved from the reaction in ether.

B. SOME INDIVIDUAL COMPOUNDS

In addition to the alkali metal and calcium cyclopentadienides noted above, the following compounds deserve brief comment.

1. Magnesium Cyclopentadienide

The original preparation of this compound (D.3,F.23) was by the thermal decomposition of the cyclopentadienyl Grignard reagent. However, it may now be obtained, potentially in very substantial quantities, by the direct reaction of magnesium with cyclopentadiene at 500–600°C. (G.35). The compound forms readily sublimable colorless crystals and can be stored under nitrogen. It is miscible in all proportions with manganese cyclopentadienide (F.23).

2. Scandium, Yttrium, and Lanthanide Cyclopentadienides

Numerous lanthanide compounds, $M(C_5H_5)_3$, have been made (F.15). They are all rather air-sensitive but are thermally very stable indeed. The chemical reactivities are similar to those of other cyclopentadienides. The magnetic susceptibilities of the paramagnetic compounds are those to be expected for the lanthanide M^{3+} ions. No X-ray studies have been made, and the relative dispositions of the anions are not known, but it was suggested that in the free molecules the rings lie perpendicular to axes directed from the metal atom to their centers, at angles of 120 degrees.

3. Manganese Cyclopentadienide

Unlike the other elements of the first transition series which give di-π-cyclopentadienyl compounds, the manganese analog, $Mn(C_5H_5)_2$, first reported by Wilkinson and Cotton (D.3) is ionic. In a subsequent comprehensive study of the compound and a comparison with the other $C_{10}H_{10}M$ compounds by Wilkinson, Birmingham, and Cotton (F.23) considerable physical and chemical evidence (see Table III) was obtained for the ionic formulation. Mass spectral studies on $MgCp_2$ and $MnCp_2$ (E.11) showed that they behaved very similarly with respect to the nature and yields of the ionic species produced in electron bombardment but that they differed strikingly from the neutral di-π-cyclopentadienyl metal compounds. The manganese compound was also shown (F.23) to possess unique magnetic properties (Section VII-B-2), being antiferromagnetic at low temperatures and with considerable spin-spin interaction up to 433°K., where a sharp magnetic transition occurred which was associated also with a change in color, from amber-brown* to the pink of the Mn^{2+} ion. Below 433°K. the crystal was rhombic, and above this temperature, to the melting point of 445–446°K., monoclinic. In the latter form, the compound has five unpaired electrons. Paramagnetic resonance studies (G.51; Section VII-B-2) have subsequently completely confirmed the ionic nature of the compound and its antiferromagnetism. In view of the similarity in vapor pressure (see Table V) and melting points of $MnCp_2$ and π-Cp_2Fe the former was considered, on electrostatic grounds, also to have (together with $MgCp_2$) the same "sandwich" configuration of ferrocene. Preliminary X-ray studies on $MnCp_2$ (E.23) and $MgCp_2$ (E.22) have indeed shown that this is the case.

4. Thallium Cyclopentadienide

This compound was first reported in the literature by Fischer (G.5). It was made by the unusual aqueous reaction (eq. 5), whereupon the compound precipitates from

$$C_5H_6 + TlOH = C_5H_5Tl + H_2O \qquad (5)$$

solution. This reaction has been suggested as an analytical method for the thallous ion (G.6).

The formulation of the compound as a cyclopentadienide by Cotton and Reynolds (H.6) is based on infrared spectral measurements, a consideration of ionization potentials, and a calculation of overlap integrals. It was concluded that while the compound has a π-cyclopentadienyl geometry (cf. $MnCp_2$), which could result from overlap of the ring e_1 orbitals with the metal e_1 (p_x, p_y) orbitals, the bonding in C_5H_5Tl is largely ionic.** The unusual thermal and chemical stability, e.g., toward air, of this compound must be due largely to an extremely stable crystal lattice, since it may be noted that the methylcyclopentadienide (I.8) is vigorously oxidized by air. Any objection to the ionic formation for TlC_5H_5 on the ground that the

---

* Amber in thin sections by transmitted light, brown by reflected light. Solutions in ethers are yellow.

** Microwave spectra of C_5H_5Tl at 100°C. by J. K. Tyler, A. P. Cox, J. Sheridan, *Nature, 183*, 1182 (1959), have confirmed this view.

TABLE I. Cyclopentadienides

Compound	m.p. (b.p.)	Color	Prep.	IR	UV	Remarks
LiCp$_{(sol)}$		colorless	E.10			
Liind$_{(sol)}$		colorless	A.13,D.2			
Lifluor		colorless	A.10,A.13			
NaCp	d. $\not<$ 300	white powder	F.5,F.23		I.13	
Naind		white powder	A.5,A.9			
Nafluor		white powder	F.6			
KCp		white powder	A.4,D.8		I.13	
CaCp$_2$		grey powder	D.1,F.5			
MgCp$_2$	176	colorless cryst.	F.23 G.35	F.23,H.6	I.13	sub. ~50 in vac.
MgCpX		colorless cryst.	A.2,A.7			
Mg ind Br		colorless cryst.	A.2, A.7			
ScCp$_3$	240	straw cryst.	F.15			sub. ~150 in vac.
YCp$_3$	295	greenish yellow cryst.	F.15			sub. ~150 in vac.
LaCp$_3$	395d.	colorless cryst.	F.15			
CeCp$_3$	435d.	orange yellow cryst.	F.15			exceed. sens. to air
PrCp$_3$	415	green cryst.	F.15		F.15	sub. ~150 in vac.
NdCp$_3$	380	reddish blue cryst.	F.15			sub. ~150 in vac.
Nd(MeCp)$_3$	165	reddish blue cryst.	F.15,I.8			sub. ~90 in vac.
SmCp$_3$	365	orange cryst.	F.15			sub. ~150 in vac.
GdCp$_3$	350	yellow cryst.	F.15			sub. ~150 in vac.
DyCp$_3$	302	yellow cryst.	F.15			sub. ~150 in vac.
ErCp$_3$	285	pink cryst.	F.15		F.15	sub. ~150 in vac.
YbCp$_3$	273	green cryst.	F.15			sub. ~150 in vac.
MnCp$_2$	172–3[a]	amber cryst.	F.23,P.21	F.23	I.13	sub. 50; sol. ethers; sp. sol. hydrocarbons
Mn(MeCp)$_2$	61–63 (85–90/1 mm.)	reddish brown cryst.	I.8,P.21			
TlCp	d. ~230	pale yellow powder	G.5	H.6		insol. H_2O
Tl(MeCp)	88–89d.	pale yellow powder	I.8			insol. H_2O
ZnCp$_2$	?	colorless	G.8[b]			

[a] Of pink form (160–73°). [b] No analysis; a white ppt. is obtained on adding $ZnCl_2$ to NaCp in THF (G. W. 1953; P.5) which does not sublime in vacuum at 250° C.

compound does not react with water, as do the other cyclopentadienides, may be met by noting that if it is indeed a high lattice energy which accounts for its stability, this would also account for its resistance to hydrolysis. The well-known case of oxides can be quoted for comparison; while the O^{2-} ion is immediately hydrolyzed by water, there are innumerable metallic oxides of predominantly ionic nature which are insoluble in and unattacked by water due to their high lattice energies.

The established cyclopentadienides (and a few substituted cyclopentadienides) are listed in Table I.

III. Di-π-cyclopentadienyl Compounds

A. GENERAL REMARKS

Essentially all* of the elements of the three series of transition metals have been shown to form di-π-cyclopentadienyl compounds of the general formula $[(\pi\text{-}C_5H_5)_2M^n]X_{n-2}$, where n is the oxidation number of metal M and X is a univalent anion. The known compounds, together with references, are listed in Table II.

The elements of the *first transitional series* (excepting Mn, *q.v.*) have been obtained as the neutral compounds, $(\pi\text{-}C_5H_5)_2M$, as well as in cationic species. For the *second* and *third transitional series*, the neutral compounds, which obviously involve the +2 oxidation state of the metal, have been obtained only for Ru and Os; it is well known that the relative stability of the lower oxidation states in these series tends to be less than that of the higher ones, but for the larger metal ions there may also be poorer overlap of the *d* orbitals of the metal with the π-orbitals of the rings leading to weaker bonding. In some cases where the preparative methods, e.g., sodium borohydride reduction of the cations or of the NaCp reaction mixture, might have been expected to lead to the neutral compound, unusual behavior has been observed and for Re, Mo, and W, di-π-cyclopentadienyl metal hydrides (see Section III-E-1) have been obtained instead; with Co and Rh, reduction of the cations $(\pi\text{-}C_5H_5)_2M^+$ with sodium borohydride has led to the cyclopentadiene compounds, e.g., $\pi\text{-}C_5H_5RhC_5H_6$. With $LiAlH_4$, however, reduction of $\pi\text{-}Cp_2Co^+$ and $\pi\text{-}Cp_2V^+$ to the neutral species has been reported (E.18).

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* Hafnium has not been reported; it will undoubtedly behave like zirconium. Technetium may be expected to give a hydride comparable to the rhenium compound (see Section III-E-1); it appears unlikely to form an ionic derivative as manganese does. Platinum has not been obtained as a di-π-cyclopentadienyl compound, but $(\pi\text{-}C_5H_5)_2Pd$ has been obtained (G. W., unpublished work, 1953) as cherry red, thermally unstable crystals. Neutron activation of π-Cp_2Ru has been reported (I.21) to give traces of a volatile rhodium compound which is probably π-$CpRHC_5H_6$ (see Section IV-D-2).

In the +3 oxidation state, cationic species, e.g., $(\pi\text{-}C_5H_5)_2Co^+$, are obtained. Salts of small anions can be occasionally obtained, e.g., $(\pi\text{-}C_5H_5)_2CoBr$, but these salts are usually very deliquescent. The ions can be precipitated from aqueous solution by large anions, e.g., silicotungstate, Reineckate, tetraphenylborate, picrate, tribromide or polyiodide, tetracarbonylcobaltate, etc. The precipitation reactions of $\pi\text{-}Cp_2M^+$ ions are very similar to those of the heavy alkalies, Rb and Cs, and the tetraphenylborate is essentially quantitatively precipitated in weakly acid solution. The first cationic di-π-cyclopentadienyl compounds characterized (B.2)—of the ferricenium ion—were the tetrachloroaluminate and tetrachlorogallate, which were obtained as long blue needle crystals by allowing solutions of ferrocene and the anhydrous metal halide in ether to stand in dry air. In the +4 and +5 oxidation states where compounds are formed (Ti and V groups), di-π-cyclopentadienyl metal halides are obtained. These have appreciable covalent character and are readily soluble in polar, and to some extent nonpolar, organic solvents. In water, hydrolysis occurs, hydrolyzed species being obtained; no systematic study of such hydrolyses has yet been made, and there is no information as to whether polymeric species are formed. The hydroxy ions which we can write, not necessarily implying this formulation, as $\pi\text{-}Cp_2TiOH^+$, $\pi\text{-}Cp_2NbOH^{2+}$(?), etc., again give precipitates with large anions; on increasing the halogen acid concentration the undissociated halides can be extracted with, say, chloroform; halogen interchanges can be effected by halogen acids.

The only di-π-cyclopentadienyl metal ions which are stable in alkaline solution are those of Co^{III}, Rh^{III}, and Ir^{III}, whose hydroxides are strong bases, absorbing carbon dioxide from air. All other cationic species are destroyed in alkaline solution.

B. PREPARATIONS

References to the preparation of individual compounds are given in Table II.

TABLE II

Di-π-cyclopentadienyl Metal Compounds

Compound	m.p.	Color	Prep.	IR	UV
Group IV					
π-Cp_2Ti	d. > 130	dark green microcryst.	F.24		
π-$Cp_2TiC_4H_8O$	81 ± 0.5	brown and green cryst. forms	F.24		
π-$Cp_2Ti^{III}{}_{aq}{}^{+}$		green	D.11		
π-$Cp_2Ti^{III}Cl_2AlEt_2$	126–30	blue cryst.	G.20		
π-Cp_2TiF_2		yellow cryst.	D.11		
π-Cp_2TiCl_2	289 ± 2	red cryst.	D.11	D.11	
π-Cp_2TiBr_2	314 ± 2	dark red cryst.	D.11	D.11	
π-Cp_2TiI_2	319 ± 3d.	purple cryst.	D.11	D.11	
π-$Cp_2TiOHBr$		orange powder	D.11		
$[\pi\text{-}Cp_2TiOH]^{+}(ClO_4)_{aq}$		yellow	D.11		
π-Cp_2TiMe_2	d. ~100	orange yellow cryst.	F.27	F.27	
π-$Cp_2Ti\phi_2$	146–48	orange yellow cryst.	E.10		
π-$Cp_2Ti(p\text{-tol})_2$	?	orange yellow cryst.	E.10		
π-$Cp_2Ti(m\text{-tol})_2$	135–40	orange yellow cryst.	E.10		
π-Cp_2Ti(*p*-methylamino-phenyl)$_2$	?	maroon	E.10		
π-$MeCp_2TiCl_2$	217–18d.	red cryst.	I.8	I.8	
π-Cp_2ZrCl_2	232	white cryst.	D.11		
π-Cp_2ZrBr_2	260d.	white cryst.	D.11	D.11	
π-$MeCp_2ZrCl_2$	180–81d.	white cryst.	I.8	I.8	

Group V					
π-Cp_2V	167–68	purple cryst.	D.20(F.23)[a]		I.13
π-$Cp_2V^{III}{}_{aq}{}^+$		purple	D.11		
π-Cp_2VCl_2	d. ~250	pale green microcryst.	D.11	D.11	
π-Cp_2VBr_2	d. ~25	dark green cryst.	D.11		
π-Cp_2NbBr_3	d. ~260	red-brown cryst.	D.11	D.11	
π-$Cp_2NbOHBr_2$		orange powder	D.11		
π-Cp_2TaBr_3	280d.	rust cryst.	D.11	D.11	
Group VI					
π-Cp_2Cr	172–73	scarlet cryst.	D.4(F.23)[a]		I.13
π-Cp_2CrI?	?	green	F.3		
[π-Cp_2Cr] [π-$CpCr(CO)_3$]	190–93	brown-black	E.24		
π-Cp_2MoH_2		yellow cryst.	I.3	I.3	
π-Cp_2MoCl_2	?	dark green cryst.	D.18	D.18	
[π-$Cp_2Mo^{IV}Cl$]$^+{}_{aq}$		red	D.18		
[π-$Cp_2Mo^{V}Cl_2$]$^+{}_{aq}$		violet	D.18		
π-Cp_2WH_2		yellow	I.3	I.3	
[π-$Cp_2W^{V}Cl_2$]$^+{}_{aq}$		red	D.18	D.18	
Group VII					
π-Cp_2ReH	161–62	lemon cryst.	E.9,I.1	I.1	
π-Cp_2ReD	168–69	lemon cryst.	I.1	I.1	
[π-Cp_2ReH_2]Cl	d. ~140	white powder	I.1	I.1	
[π-Cp_2ReD_2]Cl	d. ~140	white powder	I.1	I.1	

(continued)

TABLE II (*continued*)

Compound	m.p.	Color	Prep.	IR	UV
Group VIII					
π-Cp$_2$Fe	173 ± 0.5	orange-brown cryst.	B.1,B.9	D.5,H.19	B.2,B.4,G.43, I.13
(π-C$_5$D$_5$)$_2$Fe	?	orange-brown cryst.	H.19	H.19	
π-Cp$_2$Fe$^+{}_{aq}$ and salts		blue	B.2	D.11	B.2,G.43,G.42
π-Cp$_2$FeI$_{20}$	170–72	black powder	O.6		
π-Cp$_2$FeI$_6$	125–30d.	black needles or plates	O.6		
π-MeCp$_2$Fe	37–39 (b.p. 115/10 mm.)	orange-brown cryst.	I.8	I.8	
π-ind$_2$Fe	184–85 (H.1)	purple cryst.	D.6,C.12	D.6	D.6,C.12
(π-tetrahydroindenyl)$_2$Fe	19.5–20.5 (b.p. 126/1 mm.)	orange-red liq. and cryst.	C.12,O.16		C.12,O.16
π-Cp$_2$Ru	195–96 (B.6) 199–200 (H.4)	white cryst.	B.6	B.6,H.19	B.6
π-Cp$_2$Ru$^+$ and salts		v. pale yellow	B.6		B.6
π-ind$_2$Ru	?	white	E.25^b		
(π-tetrahydroindenyl)$_2$Ru	?	white	F.25^b		
π-Cp$_2$Os	218–19^c 230 (H.4)	white	H.4	H.4	

π-Cp$_2$Co	173 ± 1	purple cryst.	D.5,C.9		I.13
π-Cp$_2$Co$^+_{aq}$ and salts		yellow	B.7,C.7	I.3	B.7
π-Cp$_2$Co[π-CpCr(CO)$_3$]	190–93d.	brown-black	E.24		
π-Cp$_2$Co[Co(CO)$_4$]		carmine	C.7		
π-Cp$_2$Co[FeH(CO)$_4$]		rust brown	C.7		
π-MeCp$_2$Co$^+_{aq}$ and salts		wine-red	I.3	I.3	
π-ind$_2$Co	178–81	black cryst.	C.11		C.12
π-ind$_2$Co$^+_{aq}$ and salts		orange	D.6,C.11	D.6	C.12
π-Cp$_2$Rh$^+_{aq}$ and salts		yellow	C.1		C.1
π-Cp$_2$Ir$^+_{aq}$ and salts		yellow	C.1		C.1
π-Cp$_2$Ni	173d.	green cryst.	P.3,D.5,C.8	D.5,H.19	D.5,I.13
π-Cp$_2$Ni$^+_{aq}$ and salts		yellow	D.5,C.8		D.5
π-MeCp$_2$Ni	36–38 (b.p. 85–90/1 mm.)	green cryst.	I.8	I.8	
π-ind$_2$Ni(?)	d.?	red	C.11		
π-Cp$_2$Pd	d ~40	cherry red cryst.	[d]		
Tri-π-C_5H_5 compound					
π-Cp$_3$UCl	260–65	dark red cryst.	F.25	F.25	F.25

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[a] Recommended preparation.

[b] Magnetic properties mentioned only.

[c] E. R. Lippincott, quoted in E.20.

[d] G. W., unpublished work, 1953; no analysis.

Numerous preparative methods are now extant, some of use only in specific cases.

1. From Cyclopentadienides

Many of the methods are based on the use of cyclopentadienides of the alkalies, in liquid ammonia, ethers, dimethylformamide, ethanol, tertiary butanol, etc., and the transition metals are added as anhydrous halides, thiocyanates, acetylacetonates, etc. The Grignard reagent which was initially used rather widely is now seldom employed.

The most generally convenient and universally applicable method and indeed the *only method that need be employed* is the reaction of anhydrous metal chlorides (or other halides) with a solution of sodium cyclopentadienide in tetrahydrofuran or a polyether such as ethylene glycol dimethyl ether (F.23). A detailed laboratory procedure for the preparation of the reagent and of ferrocene as an example has been given (F.32); this method has the advantage that it can be used for the preparation of all types of cyclopentadienyl compounds and can be used also for nontransition metal compounds, e.g., $(C_5H_5)_2Sn$ from $SnCl_2$; for complex compounds, e.g., π-C_5H_5Rh-cycloocta-1,5-diene from $(C_8H_6RhCl)_2$; and for cyclopentadienides, e.g., $Mn(C_5H_5)_2$ from $MnCl_2$. There is no danger of solvolysis of the metal halide or other salt interfering with the preparation, as can occur using liquid ammonia or alcohols.

The reaction product, after removal of solvent ether, may be isolated by solvent extraction or in the case of air-sensitive compounds by direct sublimation from the dry residue in vacuum. The sodium in ether method is also applicable to the preparation of derivatives from methyl and other substituted cyclopentadienes, and indene.

It may be noted that unlike the reaction in liquid ammonia (Section II), hydrogen is evolved in the reaction of sodium with cyclopentadiene in ether, but some reduction ($\sim$10%) to cyclopentene occurs and yields over 90% have not been obtained, although it is known that the reaction of pure cyclopentadienides with, say, ferrous chloride, is quantitative (F.15,F.23).

Should magnesium cyclopentadienide (Section II) become commercially available, this would provide a simple method for preparing many derivatives.

2. *From Cyclopentadiene*

A method which has been applied in a few cases and is particularly convenient for the preparation of (π-$C_5H_5)_2$Fe, -Co, and -Ni is the reaction of the anhydrous halide with cyclopentadiene in an amine, such as diethylamine, pyridine, or piperidine, which acts both as solvent and as halogen acceptor (F.23), e.g., reaction 6. Again, a detailed laboratory procedure has been given (F.32); the above-noted compounds can be made in ~80% yield, while (π-$C_5H_5)_2$-Ti(Zr)Cl_2 can be got in ~50% yields.

$$FeCl_2 + 2C_5H_6 + 2\ \text{amine} = (\pi\text{-}C_5H_5)_2Fe + 2\ \text{amine}\cdot HCl \qquad (6)$$

Other less generally useful methods for preparing the (π-$C_5H_5)_2$M compounds are the reaction of $Cr(CO)_6$ and $Co_2(CO)_8$ with cyclopentadiene at elevated temperatures, the thermal decomposition of the binuclear carbonyl (Section IV), [π-$C_5H_5Fe(CO)_2]_2$, and the direct reaction of cyclopentadiene with Fe or iron oxides.

C. PHYSICAL PROPERTIES OF DI-π-CYCLOPENTADIENYL METAL COMPOUNDS

A great variety of physical measurements on the [(π-$C_5H_5)_2M^n$]-X_{n-2} compounds have been made and these are now presented in summary form. The significance of some of the measurements is discussed in more detail in Section VIII. There has been a discussion of covalence in neutral π-Cp_2M compounds in terms of valence states and electronegativities (G.34).

1. *Crystal Structures*

Of all the di-π-cyclopentadienyl compounds prepared to date, only ferrocene (F.1), ruthenocene (G.44), dibenzoylferrocene (G.37), and di(π-indenyl)iron (H.1) have been comprehensively studied by X-ray methods. Even in the case of ferrocene, further refinement by low temperature studies is desirable in view of the acknowledged motion in the lattice at room temperature. The published data on all cyclopentadienyl compounds are collected in Table III.

It is interesting to note that in contrast to ferrocene, which has the staggered configuration in the crystal (Fig. 1A), ruthenocene is eclipsed (Fig. 1B). This difference is due to differences in the lattice forces and/or to smaller van der Waals' forces when the rings are

TABLE III. Structural Data: A. Crystal Data

Compound	Ref.	Form	Space group	*a*, A.	*b*, A.	*c*, A.	β	Mol. vol., A.
π-Cp_2Fe	F.1[a,i]	monoclinic	P_{21}/a	10.561	7.597	5.952	121.02	
π-Cp_2Ru	G.44[a]	orthorhombic	62 *Pnma*	7.13	8.99	12.81		
(π-ind)$_2$Fe	H.1[a]	monoclinic	C_s^2–P_a, C_{2h}^4–P_2/a or C^5_{2h}–$P_{21}/_a$	11.32	7.85	8.09	115.3	650
π-Cp_2V	E.22	monoclinic	P_{21}/a	10.82	8.02	5.88	121.3	218
π-Cp_2Cr	F.36	monoclinic		10.74	7.89	5.93	121.2	215
π-Cp_2Fe	B.3,C.6,B.10	monoclinic		10.74	7.89	5.93	121.2	202
π-Cp_2Co	C1.4	monoclinic		10.60	7.71	5.90	121.1	206
π-Cp_2Ni	C1.4	monoclinic		10.68	7.86	5.88	121.2	211
Dibenzoylferrocene	G.37[a]	monoclinic	P_{21}/u					
Diacetylferrocene	G.37	monoclinic	P_{21}/a					
Dipropionylferrocene	G.37	monoclinic	P_{bca}					
Dibutyrylferrocene	G.37	monoclinic	*Aba*					
π-Cp_2TiCl_2	[b]	triclinic						
π-$Cp_2TiCl_2AlEt_2$	H.3,H.7		*Pnma* or *Pn2₁a*	15.77	14.24	7.54	90 (α = β = γ)	
π-Cp_2ZrCl_2	H.2[c]	monoclinic		6.20	6.58	13.33	89	
[π-$CpMo(CO)_3]_2$	F.30,G.29[a]	monoclinic	~C_{2h}–2/*m*(point) C_i–T (site)	10.3_6	7.9_6	12.0_6	125.11	
[π-$CpW(CO)_3]_2$	F.30	monoclinic	P_{21}/c	10.3_8	8.0_4	12.0_8	125.08	
[π-$CpFe(CO)_2]_2$	F.30,I.4[a]	monoclinic	P_{21}/c	7.0_8	12.4_9	8.0_1	108.1 (F.30)	
				7.0_7	12.46	7.99	108.07 (I.4)	
NaCp	F.5		powder photograph					
$MgCp_2$	E.22	monoclinic		10.98	8.04_1	5.98	121.9	224
$MnCp_2$	E.23	rhombic[d]	C_{2h}^{21}*cmma*	[28.1]	[11.7]	[9.9_5]		
bz_2Cr	F.37	cubic	*Pa*3–T_h^6	a_0 = 9.67				226

B. Distances in Sandwich Compounds

Compound	Ref.	M–C, A.	C–C, A.	Other distances, A.
π-Cp$_2$Fe	F.1	2.045 ± 0.01	1.403 ± 0.02	Inter-ring 3.32
(π-ind)$_2$Fe	H.1	2.10	1.43	
Dibenzoylferrocene[e]	G.37	2.05 ± 0.02	1.41 ± 0.03	C–C (bz) 1.39 ± 0.03 C–O 1.21 ± 0.01
π-Cp$_2$V	E.22	2.3[f]		
π-Cp$_2$Cr	F.36	2.2[f]		
π-Cp$_2$Co	C.14	2.1[f]		
π-Cp$_2$Ni	C.14	2.2[f]		
π-Cp$_2$TiCl$_2$AlEt$_2$	H.7	2.3		Ti–Cl = Al–Cl = ~2.5
[π-CpFe(CO)$_2$]$_2$	I.4	2.11 ± 0.03	1.41 ± 0.04	Fe–Fe = 2.49 Fe–C(non-br) = 1.75 Fe–C(br) = 1.85 C–O (non-br) = 1.12 C–O(br) = 1.21
π-CpNiNO[g]	H.15	2.107 ± 0.001		N–O 1.10 ± 0.03
π-Cp$_2$Fe[g]	E.14	2.03 ± 0.02	1.43 ± 0.03	C–H 1.09 (assumed) Inter-ring 3.25
bz$_2$Cr	F.37	2.19 ± 0.1[h]	1.38 ± 0.05[h]	
π-Cp$_2$Ru	G.44	2.208 ± 0.02	1.434 ± 0.03	Inter-ring 3.68

[a] Full structure determinations.

[b] D. P. Shoemaker, Massachusetts Institute of Technology, private communication.

[c] Refractive indices also given.

[d] Amber-brown form.

[e] Benzoyl groups lie out of plane of C_6H_5 ring and are displaced by rotation about C–C single bonds, which reduces steric hindrance. In crystal, molecular asymmetry corresponds to 1,2′-position.

[f] By interpolation using ferrocene as reference.

[g] Electron diffraction.

[h] Estimated by trial and error.

[i] In F.1 the z coordinates of C_1, C_2, and C_3 should be negative.

farther apart. It may be noted that in di(π-indenyl)iron, the benzene rings are in the *gauche* position, this form again being stabilized in the crystal by crystal forces or by weak van der Waals' forces between the atoms of the six-membered rings (3.43 A. apart). As with the other π-cyclopentadienyl compounds, in solution or in the vapor, the rings are probably freely rotating in the indenyl compound, or nearly so.

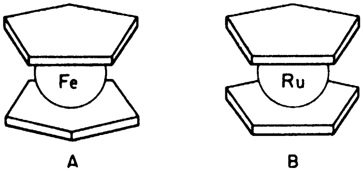

Fig. 1. Staggered and eclipsed configurations found for (A) ferrocene and (B) ruthenocene, respectively, in their crystals.

For the other neutral compounds, (π-C_5H_5)$_2$V, -Cr, -Co, and -Ni, X-ray measurements have shown that they are isomorphous with ferrocene, being monoclinic. Using ferrocene as a reference, M–C distances have been estimated for the other molecules (Table III). It is to be noted that the M–C distance for π-Cp_2Ni (2.18–2.20 A.) is considerably longer than that for π-Cp_2Fe (2.045 A.), which is consistent with the much diminished chemical and thermal stability. The only X-ray structural studies on a di-π-cyclopentadienyl metal compound other than neutral species have been recently made on the binuclear halogen-bridged compound (π-C_5H_5)$_2$TiCl$_2$Al(C_2H_5)$_2$ (H.7: Section III-E). In view of the fact that in this case the π-C_5H_5 rings were found to be *not* parallel, as in the neutral compounds, but that the metal–ring axes were at a small angle, the question may be raised as to whether in other di-π-cyclopentadienyl compounds, e.g., (π-C_5H_5)$_2$TiX$_2$ and (π-C_5H_5)$_2$ReH, where additional atoms or groups are bound to the metal, a similar situation holds. It is certainly quite possible, and further X-ray studies on this type of compound are much needed.

2. Electron Diffraction

The only published work is on ferrocene (E.14). The derived bond length data (Table III) agree well with the X-ray data and in addition suggest that rotation of the rings about the main molecular axis occurs under the high temperature conditions of the measurement.

3. Dipole Moments

The dipole moments of ferrocene and nickelocene are zero. Dipole moments of mono- and diacetylferrocenes have been reported, and the values are close to those to be expected assuming free rotation of the π-cyclopentadienyl rings about the metal–ring axis. The data and references are collected in Table IV. It has been estimated from studies on mononuclear π-cyclopentadienyl compounds (F.40) that the π-C_5H_5 metal moment is about 2–2.5 D.

TABLE IV

Dipole Moments

Compound	μ, Debyes	Ref.
π-$CpVOCl_2$	4.93 ± 0.09	H.24
π-$CpV(CO)_4$	3.17 ± 0.05 (10%)[a]	F.40
π-$CpCr(CO)_2NO$	3.19 ± 0.05 (10%)[a]	F.40
bz_2Cr	0	F.41
tol_2Cr	0	F.41
π-$CpMn(CO)_3$	3.30 ± 0.05 (10%)[a]	F.40
π-Cp_2Fe	0	B.2,F.41
Monoacetylferrocene	3.20	E.8
Diacetylferrocene	4.23	E.8
Di(p-chlorophenyl)ferrocene	3.12	G.19
Di(π-ind)Ru	0	F.41
π-$CpCo(CO)_2$	2.87 ± 0.1 (10%)[a]	F.40
π-Cp_2Ni	0	D.5
Cp_2Sn	1.02 ± 0.06	F.41
Cp_2Pb	1.63 ± 0.06	F.41
$C_{25}H_{25}Co_2$	0	F.41

[a] Indicates that atom polarization was taken as 10% of electronic polarization.

4. Mass Spectra

Measurements on neutral compounds of the elements of the first transitional series and of $(\pi\text{-}C_5H_5)_2Ru$, $(\pi\text{-}C_5H_5)_2ReH$, and $Mg(C_5H_5)_2$ have been made (E.11). The ionization potentials and appearance potentials for the various species formed in electron bombardment, e.g., $C_5H_5M^+$, were obtained. Significant differences in the behavior of the $(\pi\text{-}C_5H_5)_2M$ compounds were observed; e.g., the yields show that the ions $C_5H_5Ni^+$ and $C_5H_5V^+$ are more stable than $C_5H_5Cr^+$, -Fe^+, or -Co^+. No theoretical treatment of these differences has yet been attempted.

The mass spectra also allowed a clear distinction to be made between the π-cyclopentadienyl compounds and the cyclopentadienides $MnCp_2$ and $MgCp_2$; quite a different spectrum was obtained for the latter compounds, the yields of the ions M^+ and $C_5H_5M^+$ being very significantly higher. The higher yield of $C_5H_5V^+$ noted above is consistent with a view (G.34) that π-Cp_2V is more ionic than other sandwiches, and it may be noted also in this respect that π-Cp_2V readily forms ammoniates (F.23).

The neutral π-cyclopentadienyl compounds provide useful vehicles for the introduction of metal atoms into electron-impact-type ion sources. The natural abundances of Ru isotopes were studied in this way (C.2) and the isotopic ratios in V and Re checked (E.11).

5. *Magnetic Measurements*

Magnetic susceptibilities of essentially all of the compounds made to date have been measured. These measurements are comprehensively discussed subsequently (Section VII) together with *parahydrogen conversion* studies.

6. *Nuclear Magnetic Resonance Measurements*

Several short notes on nuclear resonance studies have appeared, but so far no substantial paper has been published.

High resolution n.m.r. measurements and chemical shifts for ferrocene and a few other π-cyclopentadienyl compounds have been given (F.27). It was found possible to distinguish between π-C_5H_5 and σ-C_5H_5 derivatives, the former giving a proton resonance on the high field side relative to the latter. The apparent relatively high diamagnetic shielding of protons in π-C_5H_5 rings (1.5–3.2 p.p.m. vs. phenyl protons in toluene) may be due to fields in filled metal *d* orbitals rather than to high electron density on the ring protons.

Wide line n.m.r. measurements have been made on ferrocene (G.33); the narrow line width (4.0 gauss) at 273°K. was said to be consistent with free rotation, or at least with considerable motion of the rings. The line was reported to decrease in width to 2.2 gauss at 194°K., perhaps owing to a second-order phase transition, and to broaden again to 4.2 gauss at 77°K. In contrast to this report of a minimum at about 194°K., other work (G.27) indicates that the line width and second moment remain constant over the range 300–110°K., suggesting no marked change in structure; the strong signals at low temperatures (a 10-fold increase in signal:noise ratio from 190 to 110°K.) were attributed to a pronounced reduction in the spin lattice relaxation time, perhaps owing to an electron transfer process. This would be in line with the well-known thermochroism of ferrocene, which changes from orange at 200°K. through yellow to a pale yellow at 77°K.

N.m.r. measurements have been made on the solid paramagnetic species (π-$C_5H_5)_2Ni$ (G.28), (π-$C_5H_5)_2V$, -Cr, -and -Co (H.10) and on manganese cyclopentadienide (H.10). In π-Cp_2Ni a shift of the proton resonance of 0.032% to higher fields is attributed to charge-transfer bonding between the metal atom and the carbon atoms of the ring. Negative charge having spin polarization opposite to that of the nickel ion is transferred from the ring to the metal. The positive spin density thus produced on the carbon atoms in turn produces negative spin density on the protons, accounting for the anomalous proton shift to higher fields. The observed shift suggests that each unpaired electron in π-Cp_2Ni is localized on the rings for a fraction of the time (~50%). For π-Cp_2V and π-Cp_2Cr, shifts of the proton resonance to *lower* applied fields were observed. This suggests spin transfer processes which leave negative spin density on the carbon atoms in this case.

The integrated spin density on the carbon atoms is estimated to be $+0.14$ in (π-$C_5H_5)_2Ni$, -0.12 in (π-$C_5H_5)_2Cr$, and -0.06 in (π-$C_5H_5)_2V$. Shifts to higher fields in $Mn(C_5H_5)_2$ and (π-$C_5H_5)_2Co$ are smaller and are comparable to bulk demagnetization effects. These observations on the paramagnetic species have been stated by McConnell* to be incompatible with the predictions of any of the theoretical treatments (Section VIII-B) of the bonding in (π-$C_5H_5)_2M$ compounds given so far.

7. *Paramagnetic Resonance Measurements*

While paramagnetic resonance signals have been quoted as being observed in (π-$C_5H_5)_2Ni$ (G.27), no data have yet been published.

* 133rd National A.C.S. Meeting, San Francisco, April, 1958.

Paramagnetic resonance studies on π-Cp_2V have recently been described (I.13). In benzene solution, a *g* value of 2.00 was found with a V^{51} isotropic hyperfine splitting equal to 77 mc. This work is discussed in Section VII-B-1.

8. *X-ray Absorption Edge Measurements*

Numerous compounds have been studied by this technique. While attempts have been made to interpret the data as showing complete filling of the available metal orbitals to give an inert gas configuration, this interpretation is suspect. This topic is discussed in more detail and references to the literature are given in Section VIII.

9. *Ultraviolet and Visible Absorption Spectra*

Numerous and scattered measurements have been made. References to the literature are given in Table II for solution measurements. Measurements on single crystals (D.14,E.5) have also been reported, but at the present time no theoretical interpretation of the spectra of any of the compounds has been accomplished.

It may be noted, however, that the original observation (B.4) that the spectrum of ferrocene in carbon tetrachloride is different from that in hydrocarbon or alcoholic solvents with a band at 325 mμ in inert solvents, apparently increasing intensity and shifting slightly to shorter wavelengths, has been studied in detail (G.43). It was shown that a new band at 307 mμ, not connected with the band at 325 mμ in inert solvents, appeared in the ferrocene spectrum in halogenated solvents and that this could be attributed to dissociative charge transfer (eq. 7). The ferricenium ion was indeed observed to

$$(\pi\text{-}C_5H_5)_2Fe + CCl_4 \xrightarrow{h\nu} (\pi\text{-}C_5H_5)_2Fe^+ + Cl^- + CCl_3\cdot \qquad (7)$$

be formed on allowing solutions of ferrocene in carbon tetrachloride to stand in light. The electron transfer spectrum absorption was found in halocarbons in alkyl halides with low C-X dissociation energies. Ferrocene and iodine showed no charge transfer spectrum but were shown to be in thermal equilibrium (eq. 8), for which

$$(\pi\text{-}C_5H_5)_2Fe + {}^3/_2\,I_2 = (\pi\text{-}C_5H_5)_2Fe^+I_3^- \qquad (8)$$

equilibrium constants were obtained in benzene, chloroform, and dichloromethane. This work provides an explanation for previous observations (O.6,O.19) on the reaction of ferrocene with iodine, in which it was claimed that ferrocene did not react and can be recovered unchanged after an hour's boiling with iodine in acetic acid (O.19) and that the addition of iodine in *any* quantity to ferrocene in a solvent gives a black powdery precipitate of stoichiometry $C_{10}H_{10}FeI_{20}$. Crystallization of the latter from acetone gave $C_{10}H_{10}FeI_6$. Both these products decomposed thermally to ferrocene and iodine; they are probably ferricenium polyiodide mixtures.

A comparison of the absorption spectrum of the ferricenium ion in solutions containing chloride ion with that in perchlorate solution showed deviations from Beer's law (G.42), which was interpreted as indicating the presence of chloride complexes such as π-Cp_2FeCl and π-$Cp_2FeCl_2^-$. This may be so, but the fact that Beer's law is not followed may also be due to the well-known hydrolytic decomposition of ferricenium salt solutions, even when quite strongly acid to give ferrocene and other decomposition products.

10. Infrared and Raman Spectra

Infrared spectra have been widely used for routine characterization of C_5H_5 derivatives, since bands characteristic of a π-C_5H_5 ring, substituted π-C_5H_5 rings, σ-C_5H_5 groups, etc., have been recognized. These designations have been rather useful in organic studies of ferrocene derivatives (see, e.g., E.20,O.32,O.54). References to routine infrared measurements are included in Table II.

Lippincott and Nelson have made the only comprehensive studies for ferrocene (and ferrocene D-10), ruthenocene, and nickelocene. These were reported preliminarily (C.5,E.12), and recently the data have been collected in a complete vibrational analysis (H.19).

11. Thermochemical Data

The vapor pressure and heats of sublimation of ferrocene have been measured and heats of combustion using standard bomb calorimetry of $(\pi$-$C_5H_5)_2Fe$ and -Ni have been determined. The vibrational spectral data referred to in the preceding paragraph have allowed the calculation of other thermodynamic constants (E.12).

The available data and references are collected in Table V. Specific heat measurements from 17 to 300°K. by G. L. Kington, Imperial College, London, have shown a transition at 164°K. This may

TABLE V
Thermodynamic Properties[a]

Ferrocene			
Heat of sublimation (solid)	(B.4)		16.81 kcal./mole
Heat of vaporization (liquid)	(B.4)		11.3 kcal./mole
Heat of fusion	(B.4)		5.5 kcal./mole
Normal b.p., 230°[b]; triple point, 173° (B.4 is in error on this.)			
Vapor pressure (liquid)	(B.4)	$\log p_{\text{mm.}}$	$= 7.615 - 2470/T$
Vapor pressure (solid)	(B.4)	$\log p_{\text{mm.}}$	$= 10.27 - 3680/T$
Standard heat of formation from elements of π-Cp_2Fe (s) (combustion)	(B.5,D.5)	ΔHf^0_{298}	= 33.8 kcal./mole
The following were obtained from spectroscopic data for π-Cp_2Fe (g)	(E.12)	$\Delta Hf^0_{298.16}$	= 50.61 kcal./mole
		$\Delta Ff^0_{298.16}$	= 75.97 kcal./mole
		$\Delta Sf^0_{298.16}$	= −85.07 cal./mole
		ΔHf^0f^0	= 57.5 kcal./mole
For Cp°, $H^0 - E_0{}^0/T$, $-F^0 - E_0{}^0/T$ and S^0 from 298.16 to 1500°K., see E.12.			
Ruthenocene			
For Cp^0, $H^0 - E_0{}^0/T$, $-F^0 - E_0{}^0/T$ and S^0 from 298.16 to 1500°K., see E.12.			
Nickelocene			
Standard heat of formation from elements of π-Cp_2Ni(s) (combustion)	(D.5)	ΔHf^0_{298}	= 62.8 kcal./mole
The following were obtained from spectroscopic data for π-Cp_2Ni(g)	(E.12)	$\Delta Hf^0_{298.16}$	= 79.61 kcal./mole
		$\Delta Ff^0_{298.16}$	= 103.80 cal./mole
		$\Delta Sf^0_{298.16}$	= −81.10 cal./mole
		ΔHf^0f^0	= 85.9 kcal./mole (H.19)
For Cp^0, $H^0 - E_0{}^0/T$, $-F^0 - E_0{}^0/T$ and S^0 from 298.16 to 1500°K., see E.12.			
Dibenzenechromium			
Standard heat of formation from elements of $(C_6H_6)_2Cr$(s) (combustion)	(I.9)	ΔHf^0_{298}	= 21 ± 8 kcal./mole
$(C_6H_6)_2Cr$(s) (combustion)	(I.23)	ΔHf^0_{298}	= 51 kcal./mole
Manganese cyclopentadienide			
Heat of sublimation (solid)	(F.23)		17.3 kcal./mole
Heat of vaporization (liquid)	(F.23)		12.0 kcal./mole
Heat of fusion	(F.23)		5.3 kcal./mole[c]
Vapor pressure (solid)	(F.23)	$\log p_{\text{mm.}}$	$= 10.58 - 3780/T$
Vapor pressure (liquid)	(F.23)	$\log p_{\text{mm.}}$	$= -5.93 - 2615/T$

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[a] Some heats of sublimation recently reported by J. F. Cordes and S. Schreiner (*Z. anorg. u. allgem. Chem.*, *299*, 87 (1959)) appear to be in error because their experimental conditions make their use of the Knudsen equation inappropriate (G. L. Kington, private communication).

[b] The value of 249° in B.4 is in error (according to equilibrium still measurements—E. O. Brimm, private communication).

[c] F.23 is in error on this.

account for the fact that crystals of ferrocene (and nickelocene) explode on cooling to 90°K. (G. W., 1954, unpublished).

12. Exchange and Radiochemical Studies

It was shown that in aqueous ethanol over a period of twelve months there is no exchange between iron atoms of ferrocene and ferrous ions (F.23). This observation has been confirmed recently (H.13) and it was also shown that the electron transfer exchange between $10^{-4}M$ solutions of ferrocene and the ferricenium ion was complete within a few seconds at room temperature. Studies of the Szilard-Chalmers effect in neutron-bombarded ferrocene were also made (H.13). About 12% of the Fe^{59} formed is retained in ferrocene; this value may be increased to ~21% by heating after the bombardment. A dependence on the fraction of fast neutrons present was noted; fast neutrons are held to rupture the π-C_5H_5 rings in the molecule to form $C_5H_5\cdot$ and other organic radicals by breakdown. In more recent work (H.30) the distribution of Fe^{59} in irradiated ferricenium picrate has been studied and discussed.

Although cyclopentadiene itself exchanges rapidly with D_2O in basic solution, there is no exchange with ferrocene at ordinary temperatures (F.14). The deuteroferrocene studied by Lippincott and

TABLE VI
Oxidation-Reduction Potentials

	E⁰, volts *vs.* SCE		
Reaction	Oxid.	Red.	Ref.
$\pi\text{-Cp}_2\text{Ti}^+ = \pi\text{-Cp}_2\text{TiOH}^+_{aq} + e$	−0.44	−0.44	D.11
$\pi\text{-Cp}_2\text{V}^+ = \pi\text{-Cp}_2\text{V}^{2+}_{aq}\ (?) + e$		−0.32	D.11
$\pi\text{-Cp}_2\text{Nb}^{?+} = \pi\text{-Cp}_2\text{NbOH}^{2+}\ (?)$		−0.44	D.11
		−0.71	
$\pi\text{-Cp}_2\text{Fe} = \pi\text{-Cp}_2\text{Fe}^+ + e$	+0.31[a]	+0.30[a]	B.8
		+0.16	
$\pi\text{-MeCp}_2\text{Fe} = \pi\text{-MeCp}_2\text{Fe}^+ + e$	+0.38[a]		I.8
$\pi\text{-Cp}_2\text{Ru} = \pi\text{-Cp}_2\text{Ru}^+ + e$	+0.26[a]	+0.22[a]	B.8
		+0.11	
$\pi\text{-Cp}_2\text{Co}(?) = \pi\text{-Cp}_2\text{Co}^+_{aq} + e$		−1.16	B.8
$(\pi\text{-ind})_2\text{Co}(?) = (\pi\text{-ind})_2\text{Co}^+_{aq} + e$		−0.6	D.6
$\pi\text{-Cp}_2\text{Rh}(?) = \pi\text{-Cp}_2\text{Rh}^+_{aq}$		−1.53	
$\pi\text{-Cp}_2\text{Ni} = \pi\text{-Cp}_2\text{Ni}^+ + e$	−0.08[a]	−0.21	D.5

[a] In 90% ethanolic supporting electrolyte.

Nelson (H.19) was prepared by treating ferrocene with $Ca(OD)_2$ at high temperatures, the method used for deuterating benzene and other hydrocarbons.

13. Oxidation-Reduction Potentials

The available data and references are collected in Table VI.

D. SOME CHEMICAL PROPERTIES

1. Neutral Compounds, π-Cp_2M

The compounds of Ti, V, Cr, Fe, Co, and Ni are all soluble in hydrocarbon solvents and readily sublimable in vacuum. The titanium compound is thermally unstable, decomposing before melting at ~140° and the nickel compound melts at 173° with extensive decomposition. Only ferrocene is stable in air; the others are attacked at various rates, π-$Cp_2Ni \ll \pi$-$Cp_2V < \pi$-$Cp_2Cr < \pi$-Cp_2Ti, and the V, Cr, and Ti compounds must be handled in vacuum or in an inert atmosphere. π-Cp_2Ni is moderately stable in air, decomposing only over a period of a day or two in the solid state and somewhat faster in solution.

The action of various agents on the neutral compounds was surveyed during studies on manganese cyclopentadienide (F.23); these, together with a few additional reactions, are listed in Table VII. The compound π-Cp_2Cr was shown to behave to some extent like a cyclopentadienide in that it readily formed several ammoniates and also reacted with ferrous chloride in tetrahydrofuran to give almost a 50% yield of ferrocene together with a green halide species, which has not yet been characterized properly, but undoubtedly has only one π-C_5H_5 ring per metal atom. The vanadium compound, π-Cp_2V, also behaved to some extent as an ionic derivative in forming ammoniates, as do π-Cp_2Cr and $MnCp_2$; with ferrous chloride, small amounts of ferrocene were obtained, but the compound was mainly oxidized to the di-π-cyclopentadienylvanadium cation. It may be remembered that Skinner and Summer (G.34) have subsequently also suggested that π-Cp_2V has some ionic character; but from the point of view of chemical reactivities, this is certainly less than for π-Cp_2Cr. It has been reported recently (H.33) that π-Cp_2TiCl_2 reacts with $TiCl_4$ to give π-$CpTiCl_3$. The neutral compounds of V, Mn, Co, and Ni, reacting with either CO or NO, can also lose one ring to give carbonyls or nitrosyls (Section IV-B). Following the demonstration of aromatic reactivity in *ferrocene* (O.0) a comprehensive chemistry of the compound has developed; since this work is primarily organic in nature it will not be discussed here. The early studies were reviewed by Pauson (E.20), and there is a more recent review by Rausch, Vogel, and Rosenberg (G.25).

The only other neutral compounds for which aromatic substitution reactions have been reported (H.4) are $(\pi\text{-}C_5H_5)_2Ru$ and $(\pi\text{-}C_5H_5)_2Os$, (although it has been shown that one of the more stable mono-π-cyclopentadienyl compounds, viz., $\pi\text{-}C_5H_5Mn(CO)_3$ (Section IV), undergoes aromatic substitution reactions); $(\pi\text{-}C_5H_5)_2Ni$ might be found to react if mild enough conditions are maintained.

2. *Derivatives of* M^{III}

As noted in Section III-A, cations of this type behave as large alkali ions, although the simple salts, where known, are decidedly more prone to hydration than alkali metal salts, and the ions in solution are presumably heavily hydrated. No ion exchange distribution studies or attempts to compare the hydrated ionic radii of the $(\pi\text{-}C_5H_5)_2M^+_{aq}$ ions with those of the alkali ions have yet been made, although these are quite feasible experiments.

The ions $\pi\text{-}Cp_2Co^+$, $\text{-}Rh^+$, $\text{-}Ir^+$, and $\text{-}Ru^+$ appear to be stable indefinitely in aqueous solution. The $\pi\text{-}Cp_2Fe^+$ ion is moderately stable in acid solutions, but even here it hydrolyzes considerably, giving rise to ferrocene, and is eventually decomposed. The ions $\pi\text{-}Cp_2Ti^+_{aq}$ and $\pi\text{-}Cp_2V^+_{aq}$ are oxidized by dilute acids and are much more easily oxidized in air. The ion $\pi\text{-}Cp_2Ni^+_{aq}$ is thermally unstable in solution and is also decomposed slowly by air and rapidly by base.

The cobalt, rhodium, and iridium cations alone are stable in basic solution and the hydroxides, which have not been obtained except in solution, are strong bases absorbing carbon dioxide from the air to give carbonates in solution.

While most of these cationic species have been well characterized, although in some cases salts have not been analyzed, the nature of chromium species is still not settled. The action of aqueous acids on $\pi\text{-}Cp_2Cr$ produces cyclopentadiene, together with a deep blue (in

TABLE VII

Some Reactions of $(\pi\text{-}C_5H_5)_2M$ Compounds

	π-Cp_2Ti	π-Cp_2V	π-Cp_2Cr	$MnCp_2$[a]	π-Cp_2Fe	π-Cp_2Co	π-Cp_2Ni
Thermal stability[b]	d. ~135°	st. 300°	st. 300°	st. 300°	st. 400°	st. 250°	d. 173°
Reagent							
H_2O (air-free)	insol.	insol.	slow attack	effervesces → C_5H_6 + $Mn(OH)_2$	insol.	insol.; v. slow oxid. π-Cp_2Co^+	insol.
3*N* HCl	oxid. π-Cp_2Ti^+ π-Cp_2TiOH^+	oxid. π-Cp_2V^+ π-Cp_2V^+	gives C_5H_6 + blue soln.	C_5H_6 + Mn^{++}	insol.	slow oxid. π-Cp_2Co^+	insol.
2–3*N* HNO_3	oxid. π-Cp_2Ti^+ π-Cp_2TiOH^+ + decomp.	oxid. π-Cp_2V^+ π-Cp_2V^{2+} + decomp.	decomp. + some C_5H_6	C_5H_6 + Mn^{++}	oxid. π-Cp_2Fe^+	oxid. π-Cp_2Co^+	oxid. π-Cp_2Ni^+ + decomp.
Liquid NH_3	insol.	gives ammoniates	gives ammoniates	gives ammoniates	insol.	insol.	insol.
$FeCl_2$ in THF	no reaction	oxid. to cations; trace of ferrocene	~40% yield ferrocene + green soln.	100% yield ferrocene		oxid. to π-Cp_2Co^+	no reaction

CO (100–200 atm., 50–200° C.)		π-$CpV(CO)_4$	$Cr(CO)_6$ [π-$CpCr(CO)_3]_2$	π-$CpMn(CO)_3$	no reaction	π-$CpCo(CO)_2$	$Ni(CO)_4$
NO (1 atm.)		decomp.	+ HCl → $Cp(NO)_2Cl$	$Cp_3Mn_2(NO)_3$	no reaction		π-CpNiNO
I_2			π-Cp_2CrI(?)		π-Cp_2FeI_n (black)		
Br_2 (in CCl_4)					green expl. π-Cp_2Fe^+-Br_3^-(?) (cold); cyclo-C_5Br_6 (warm)	π-Cp_2Co^+-Br_3^-	
Color in petrol.	green	purple	scarlet	sp. sol.	orange-yellow	purple-red	green
Color in THF	green	purple	bluish red	yellow-amber	orange-yellow	purple-red	green

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[a] Does not react with CO_2, unlike $MgCp_2$.

[b] St. = stable to at least the temp. stated.

3-6*N* HCl) solution. It seems likely that the aqueous species, in contrast to the statement made by Pauson (E.20) even though evidence to the contrary was available (D.4), does not contain a di-π-cyclopentadienylchromium cation. Although the species have not been characterized properly, the liberation of cyclopentadiene on treating π-Cp_2Cr with acids, together with the fact that its reaction in tetrahydrofuran solution with ferrous chloride gives a high yield of ferrocene, strongly indicates that one C_5H_5 ring is being lost. It may be noted, too, that with ethyl iodide, π-Cp_2Cr reacts to give blue crystals of a binuclear halogen-bridged complex. Also, from the reaction of MgCpBr with chromic acetylacetonate, a compound containing only one π-C_5H_5 ring bound to the metal (Fig. 2) has been isolated and characterized (F.12). This compound dissolves in 6*N* HCl to give a deep blue solution which is probably the same as that obtained from π-Cp_2Cr. The blue aqueous species can be oxidized by air to a yellow-brown complex cation which may well be a Cr^{III} species of the type [π-$CpCr(H_2O)_nCl]^+$; it may be noted that very recently a brown-yellow aqueous species, [benzyl $Cr^{III}(H_2O)_5]^{2+}$, has been characterized (G.18). The action of excess iodine on π-Cp_2Cr has been alleged to give π-Cp_2CrI (F.3), but this work has not been confirmed yet; it seems a little surprising in view of the propensity of other π-Cp_2M^+ ions to give polyiodides that excess iodine here gives a simple monoiodide. A black complex [π-Cp_2Cr][π-$CpCr(CO)_3$] has also been claimed (E.24).

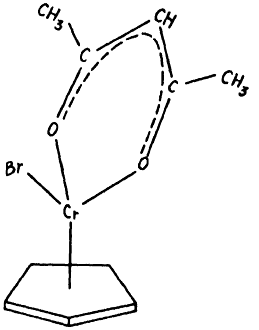


Fig. 2. The presumed structure of π-$CpCrBr^+$ acetylacetonate.

The whole question of π-cyclopentadienylchromium species, other than π-Cp_2Cr itself and the carbonyl and nitrosyl compounds (Section IV), needs further examination.

3. *Derivatives of M^{IV} and M^{V}*

The simple di- and trihalides of di-π-cyclopentadienyl compounds of Ti^{IV}, Zr^{IV}, V^{IV}, Nb^{V}, and Ta^{V} have been characterized. As noted in the introductory paragraphs, hydroxy species undoubtedly exist but need further characterization. Hydrolysis of π-Cp_2NbBr_3 in air gives a well-defined orange compound, π-$Cp_2Nb(OH)Br_2$, however.

The only molybdenum and tungsten di-π-cyclopentadienyl species are the hydrides (see Section III-E), the halide π-Cp_2MoCl_2, and the complex halides [π-$Cp_2Mo^{IV}Cl$]$^+$, [π-$Cp_2Mo^{V}Cl_2$]$^+$, and [π-$Cp_2W^{V}Cl_2$]$^+$, which can be precipitated with large anions from acid solutions.

E. SOME PARTICULAR COMPOUNDS AND TOPICS

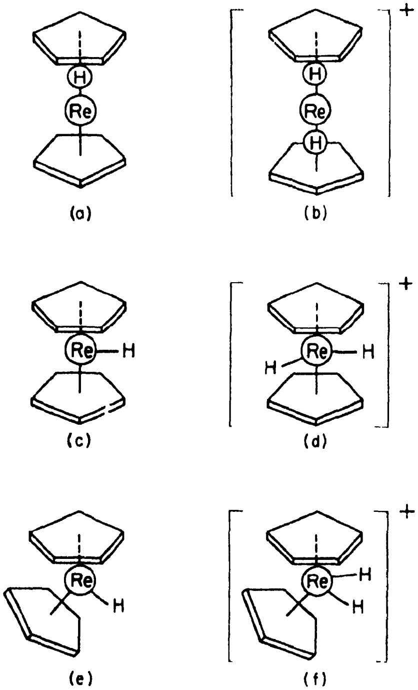
1. *The Di-π-cyclopentadienyl Hydrides of Re^{III}, Mo^{IV}, and W^{IV}*

While the formation of a π-cyclopentadienylrhenium compound, rather than an ionic derivative like $Mn(C_5H_5)_2$, was anticipated from the general chemical behavior of rhenium, the only di-π-cyclopentadienylrhenium compound so far obtained is the unusual hydride (π-$C_5H_5)_2ReH$ (E.9,I.1). This compound is obtained by the action of sodium borohydride on the tetrahydrofuran reaction mixture of NaC_5H_5 with $ReCl_5$; it may also be obtained in lower yields by merely heating the mixture without the addition of borohydride, the hydrogen presumably coming either from breakdown of the solvent or from cyclopentene or excess cyclopentadiene in the reagent.

The nature of the compound was conclusively demonstrated by high resolution nuclear magnetic resonance studies. These showed the presence of an exceedingly diamagnetically shielded proton. The splittings of the resonance peaks and the difference between the hydride and the deuterated compound π-Cp_2ReD and the cations π-$Cp_2ReH_2^+$ and π-$Cp_2ReD_2^+$ indicated that the single proton could not be located between the metal atom and the π-cyclopentadienyl ring (Fig. 3*a* or *b*), as had been suggested by Liehr (G.40), but must be as in Fig. 3*c–f*. With acids, either aqueous or anhydrous, the compound behaves as a base somewhat weaker than ammonia (eq. 9).

$$(\pi\text{-}C_5H_5)_2ReH \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} [(\pi\text{-}C_5H_5)_2ReH_2]^+ \tag{9}$$

The simple halide π-Cp_2ReH_2Cl, which is exceedingly deliquescent, as well as insoluble precipitates, e.g., the Reineckate, were also obtained.



(a) (b) (c) (d) (e) (f)

Fig. 3. Possible structures of π-Cp_2ReH and $[\pi\text{-}Cp_2ReH_2]^+$.

By the sodium borohydride reduction of the products from the reaction of $MoCl_5$ and WCl_6 with C_5H_5Na in tetrahydrofuran, yellow sublimates have been obtained and shown by nuclear magnetic resonance studies to be the dihydrides $(\pi\text{-}C_5H_5)_2MoH_2$ and $(\pi\text{-}C_5H_5)_2$-WH_2 (I.3). Unlike the rhenium compounds, these have no basic properties but dissolve in dilute acid to give a solution containing cations.

2. Di-π-cyclopentadienyltitanium Aryls and Methyl

By the reaction of lithium aryls on $(\pi\text{-}C_5H_5)_2TiCl_2$ a number of aryl derivatives, $(\pi\text{-}C_5H_5)_2TiR_2$, were prepared (E.10); these are listed in Table II. A thermally very unstable methyl compound, $(\pi\text{-}C_5H_5)_2Ti(CH_3)_2$, has also been isolated (F.27).

While it might be expected that similar alkyls or aryls would be obtained from $(\pi\text{-}C_5H_5)_2ZrCl_2$, $(\pi\text{-}C_5H_5)_2NbBr_3$, or $(\pi\text{-}C_5H_5)_2TaBr_3$, no attempts to prepare such compounds have yet been reported.

3. Di-π-cyclopentadienyltitanium(III) Aluminum Alkyl Halides

In connection with low temperature polymerization studies of ethylene, a compound of stoichiometry $(\pi\text{-}C_5H_5)_2TiCl_2\cdot Al(C_2H_5)_2$ was isolated (G.20). The X-ray structure of this compound has been given in a preliminary note (H.7), and it was found that the $\pi\text{-}C_5H_5$ rings are not parallel to each other as in ferrocene, but are at an angle (Fig. 4). The alkyl groups are bound to the aluminum atom and the titanium, aluminum, and two bridging chlorine atoms form a square with the Ti^{III}–Cl and Al–Cl distances both being ~2.5 A.*

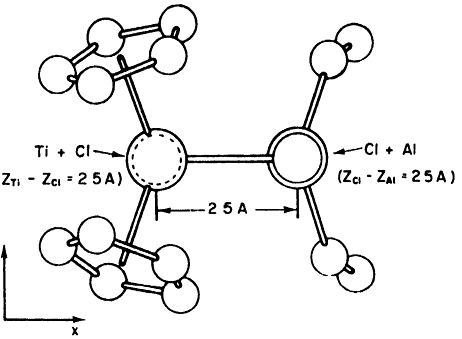


Fig. 4. The molecular structure of $(\pi\text{-}C_5H_5)_2TiCl_2\cdot Al(C_2H_5)_2$ according to X-ray studies (H.7; reproduced by permission).

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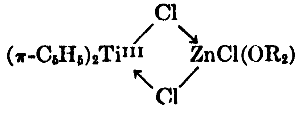
* It is possible that complexes of similar structure are present in the easily oxidized deep blue solutions obtained (G. W., unpublished observation, 1953) by treating tetrahydrofuran or acetone solutions of $(\pi\text{-}C_5H_5)_2TiCl_2$ with Zn, e.g.,



$$(\pi\text{-}C_5H_5)_2Ti^{III}\begin{smallmatrix} \nearrow Cl \searrow \\ \nwarrow Cl \swarrow \end{smallmatrix} ZnCl(OR_2)$$

This insoluble blue complex is believed to be the active catalyst in the heterogeneous polymerization of ethylene (G.20,G.15) and is formed on mixing (π-$C_5H_5)_2TiCl_2$ and triethylaluminum in hydrocarbon solvents. It is not so effective as Ziegler-type catalysts.

A more effective catalytic system, also based on (π-$C_5H_5)_2TiCl_2$, has been discovered by Breslow and Newburg (G.22). These workers also isolated the blue complex noted above but from a mixture of (π-$C_5H_5)_2TiCl_2$ with $(C_2H_5)_2AlCl$. They showed that *fresh* solutions of these components in inert hydrocarbons provide a catalytic system for ethylene polymerization quite as effective as Ziegler catalysts. They also observed that the admission of a little oxygen to the blue complex also increases its activity. The polyethylene produced in this homogeneous system is more linear and of higher melting point than Ziegler polyethylene. More detailed studies have now been reported (I.27,I.28).

4. *Miscellaneous Topics*

(a) The toxicity of *ferrocene* has been reported. It is lethal in rats at a concentration of 1000 mg. per kilogram of body weight. This may be compared to the figure of 17.5 mg. for $Fe(CO)_5$. Only slight cumulative effects were noted (E.1).

(b) *Ferrocene* has been used as a catalyst in the redox polymerization of styrene (G.38), and the effect of di-π-cyclopentadienyl compounds in vinyl polymerizations has been studied (G.31). Copolymerizations of *trans*-cinnamoylferrocene with various vinyl and other monomers have been noted (H.14).

(c) One of the few uses of ferrocene reported in trade literature is as a combustion catalyst for fuel oils and solids. Ferrocene does behave as an antiknock agent in gasolines, but oxide production limits its utility. Mention has been made (G.32) of the electrolysis of π-Cp_2TiBr_2 in various solvents.

(d) A curious compound of stoichiometry $C_{25}H_{25}Co_2$ has been sketchily reported (F.2); it is stated to be formed by the reaction of cobalticenium salts with cyclopentadienides and to be diamagnetic in the solid state, paramagnetic in solution. Its dipole moment is zero (Table IV). At the present time no details have been presented, and the nature of the compound must be said to be unknown.

F. TRI-π-CYCLOPENTADIENYLURANIUM(IV) CHLORIDE, $(\pi\text{-}C_5H_5)_3UCl$

This compound is included in this section for convenience. It is the only known case so far where three π-cyclopentadienyl rings are bound to a metal (F.25). The compound is very readily oxidized by air, but dissolves in air-free water to give yellow solutions which give insoluble precipitates with large anions as do the di-π-cyclopentadienyl cations. The formulation as a π-cyclopentadienyl compound was based on the failure of the compound to react with ferrous chloride, even for a week in boiling tetrahydrofuran and with maleic anhydride. The structure proposed for this ion (Fig. 5) is similar to that proposed for the tricyclopentadienides of the lanthanides except for the difference in the nature of the bonding. The nature of the bonding is discussed in Section VIII-B-3.

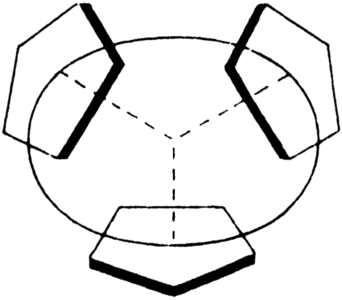


Fig. 5. Proposed structure for $[\pi\text{-}Cp_3U]^+$ (F.25; reproduced by permission.)

IV. Mono-π-cyclopentadienyl Carbonyl, Nitrosyl, and Related Compounds

A. GENERAL REMARKS

Since the first preparation by Wilkinson (D.4) of the binuclear cyclopentadienyl carbonyl compounds of molybdenum and tungsten, a large number of different types of compound with only one $\pi\text{-}C_5H_5$ ring per metal atom have been described (see Table VIII). These may be classified as follows:

1. π-Cyclopentadienyl metal carbonyls and nitrosyls: e.g., $\pi\text{-}CpMn(CO)_3$, $\pi\text{-}CpCr(NO)_2Cl$, $\pi\text{-}CpMo(CO)_2NO$.

TABLE VIII
Mono-π-cyclopentadienyl Compounds

Compound	m.p.	Color	Prep.	IR	UV
Group IV					
π-$CpTiCl_3$	~185d.	yellow prisms	H.33	H.33	
Group V					
π-$CpV(CO)_4$	138d.	orange-pink cryst.	P.21,D.20[E.15]	E.15,E.16	
π-$CpV(CO)_3Na_2[K_2]$	?	?	G.8		
π-$CpVOCl_2$	subl.	black cryst.	H.24		
Group VI					
π-CpCrBr(acetylac)	190d.	dark green cryst.	F.12		
π-$CpCr(CO)_3H$	57–58(E.24) 57.5 (P.5)	yellow cryst.	P.21,E.24(F.27^a)		
π-$CpCr(CO)_3CH_3$		yellow cryst.	F.27	F.27	
π-$CpCr(CO)_2NO$	67–68	orange cryst.	E.27		
π-$CpCr(NO)_2Cl$	d. ~140	greenish yellow cryst.	F.22,F.27	F.22	
Br	140.4–141	dark brown cryst.	F.22,F.27	F.22	
I	149–51	black cryst.	F.27		
CNS	165d.	green cryst.	F.22	F.22	
CH_3	82.2–83.2	dark green cryst.	F.27^a	F.27	F.27
CH_2Cl		green cryst.	F.27	F.27	
C_2H_5	oil	green	F.27	F.27	
C_6H_5	oil	green	F.27	F.27	
σ-C_5H_5	66.5–67.2	brown cryst.	F.27^a	F.27	F.27
$[\pi\text{-}CpCr(NO)_2H_2O]^+$ and salts		yellow	F.22		
$[\pi\text{-}CpCr(CO)_3]_2{}^b$	163–68d.	blue-green cryst.	P.21,E.21,E.24		

[π-CpCr(CO)$_3$]$_2$Hg	?	yellow powder	E.21		
[π-CpCr(CO)$_3$][π-Cp$_2$Co]	?	violet-brown	E.21		
[π-CpCr(CO)$_3$][π-Cp$_2$Cr]	190–93d.	brown-black	E.21		
[π-CpCr(CO)$_3$][bz$_2$Cr]	215–16d.	green cryst.	E.21		
π-CpMo(CO)$_3$H	54(E.21)	pale yellow cryst.	P.21,E.21(F.27^a)	F.27	
Cl	d. 145	red cryst.	F.27	F.27	
Br	150–51	red cryst.	F.27	F.27	
I	134–34.5	dark red cryst.	F.27	F.27	
CH$_3$	124d.	yellow cryst.	F.27^a	F.27	F.27
C$_2$H$_5$	77.5–78.5d.	yellow cryst.	F.27^a	F.27	F.27
iso-C$_3$H$_7$	29–30	yellow cryst.	F.27^a	F.27	
π-CpMo(CO)$_3$Na		white powder	E.21(F.27)		
π-CpMo(CO)$_2$NO	85.2–85.7	orange cryst.	F.27,E.27	F.27	
[π-CpMo(CO)$_3$]$_2$^{b}	215–17	purple cryst.	D.4,F.27	D.4,E.16	
[π(MeCp)Mo(CO)$_3$]$_2$	146–47d.	purple cryst.	I.8	I.8	
[π-CpMo(CO)$_3$]$_2$Hg		yellow powder	E.2		
π-CpW(CO)$_3$H	69	lemon cryst.	P.21,E.21(F.27^a)	F.27	
CH$_3$	144–45.3	lemon cryst.	F.27^a,E.21	F.27	F.27
C$_2$H$_5$	93.0–93.5	yellow cryst.	F.27^a,E.21	F.27	F.27
Na		white powder	E.21(F.27)		
π-CpW(CO)$_2$NO	105–7	orange	E.27		
[π-CpW(CO)$_3$]$_2$	240–42d.	purple	D.4	D.4,E.16	
[π-CpW(CO)$_3$]$_2$Hg		yellow powder	E.21		

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[a] n.m.r. also given.

[b] The stoichiometry of this compound was originally given as C$_{10}$H$_{10}$Cr$_2$(CO)$_5$ (D.15) as was the molybdenum analog (D.4); these were later corrected by the respective authors (E.24,F.27).

(*continued*)

TABLE VIII (*continued*)

Compound	m.p.	Color	Prep.	IR	UV
Group VII					
π-$CpMn(CO)_3$	76.8–77.1	yellow cryst.	E.15,D.21,P.21	E.15	F.27^a
π-$MeCpMn(CO)_3$	1.7–2.0 (I.8)^c (b.p. 112°/10 mm.)	yellow cryst.	I.8,P.21^a	I.8	
π-$indMn(CO)_3$	50–51	orange cryst.	P.21		
π-$acetylCpMn(CO)_3$	39.5–40.0	yellow	I.14	I.14	
$[\pi\text{-}CpMn(CO)_2NO]^+{}_{aq}$		yellow	E.15		
$[\pi\text{-}CpMn(CO)_2NO]_2PtCl_6$	d. ~170	yellow cryst.	E.15	E.15	
π-$Cp(\sigma\text{-}Cp)Mn(NO)_2.Mn(\pi\text{-}Cp)(NO)$	d. > 100	purple-black cryst.	F.22	F.22	F.27
$[\pi\text{-}CpMn(NO)S_2]_x$		black cryst.	F.16	F.16	
π-$CpRe(CO)_3$	104–5	white	I.2,H.25^d	I.2,^{a},H.25	
π-$CpRe(CO)_2(C_5H_6)$	111–12	v. pale yellow	I.2, G.53^e	I.2^a	
π-$CpRe(CO)_2(C_5H_8)$	95–96	white	I.2	I.2^a	
Group VIII					
π-$CpFe(CO)_2Cl$	d. 87	red cryst.	E.15	E.15	
Br	105–7	dark red cryst.	E.17		
I	119–20d.	black cryst.	F.22,F.27	F.22	
CN	d. 120	yellow cryst.	E.15		
CH_3	78–82	caramel cryst.	F.27^a	F.27	F.27
C_2H_5	oil	caramel	F.27	F.27	
C_6H_5	26–30	caramel cryst.	F.27	F.27	
σ-Cp	46	orange cryst.	E.6,^{c}F.27^a	F.27	F.27
$SiMe_3$	70	orange-yellow needles	F.31	F.31	
Na		light yellow powder	E.28(F.27)		
$[\pi\text{-}CpFe(CO)_2H_2O]^+{}_{Aq}$		yellow	E.15,F.27		
$[\pi\text{-}CpFe(CO)_2]_2$	194	red-purple cryst.	E.15,E.17	E.15	

$[\pi\text{-(MeCp)Fe(CO)}_2]_2$	98–99	deep red cryst.	I.8	I.8
$[\pi\text{-(EtCp)Fe(CO)}_2]_2$	61–62d.	purple cryst.	H.12	H.12
$[\pi\text{-indFe(CO)}_2]_2$	198d.	brownish purple cryst.	H.12	H.12
$[\pi\text{-tetrahydroindFe(CO)}_2]_2$	148d.	purple cryst.	H.12	H.12
$[\pi\text{-CpFe(CO)}_2]_2\text{Hg}$	d. 80–90	golden	E.28	
$\pi\text{-CpCo(CO)}_2$	−22 (b.p. 75/22 mm.; 140/710 mm.)	dark red	E.15,E.26	E.15,E.16
$\pi\text{-CpCo(C}_6\text{H}_6)$	98–99	wine-red cryst.	I.3	I.3[a]
$\pi\text{-MeCpCo(C}_6\text{H}_5\text{CH}_3)$	−10 (b.p. 50/10^{-3} cm.)	wine-red oil and cryst.	I.3	I.3[a]
$\pi\text{-CpRh(C}_5\text{H}_6)$	121–22	orange-yellow cryst.	I.3	I.3[a]
$\pi\text{-CpRhC}_8\text{H}_6$ (cycloocta-1,5-diene)	108–8.5	yellow cryst.	G.30	
π-CpNiNO	−41 (b.p. 49/27 mm.; 144/715 mm.)	dark red	E.15[f],E.27	E.15,E.16
π-CpNi(CO)I	d > 20	black-violet	H.27	
$[\pi\text{-CpNiCO}]_2$	d ~139	purple-red	H.27	
$\text{Cp}_3\text{Ni}_3\text{(CO)}_2$		dark green	H.27	
$\text{C}_{25}\text{H}_{25}\text{Co}$	?	red	F.2	

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[a] n.m.r. also given.

[b] The stoichiometry of this compound was originally given as $\text{C}_{10}\text{H}_{10}\text{Cr}_2\text{(CO)}_6$ (D.15) as was the molybdenum analog (D.4); these were later corrected by the respective authors (E.24,F.27).

[c] P.21 gives m.p. −0.75°, n^{22} = 1.5873; d_{20} = 1.3942; vapor press. 8 mm./100°C., 360.6 mm. 200°C.; b.p. 106°/12 mm. As shown in I.8, careful separation of C_5H_6 and C_6H_8 is necessary; sample in P.5 may not be pure.

[d] H.25 gives color as yellow and m.p. 111–14; the compound was probably contaminated.

[e] Compound wrongly formulated.

[f] n m.r. given in F.27.

2. π-Cyclopentadienyl metal carbonyl or nitrosyl halides or other salts, hydrides, alkyls, and aryls, etc.: e.g., π-$CpFe(CO)_2Cl$, π-$CpFe(NO)_2SCN$, π-$CpMo(CO)_3H$, π-$CpW(CO)_3CH_3$, π-$CpFe(CO)_2Si(CH_3)_3$.

3. Binuclear π-cyclopentadienyl metal carbonyls: e.g., $[\pi\text{-}CpFe(CO)_2]_2$, $[\pi\text{-}CpW(CO)_3]_2$.

4. π-Cyclopentadienyl metal olefin compounds: e.g., π-$CpCo(C_5H_6)$, π-$CpRh(C_8H_6)$, π-$CpRe(CO)_2(C_5H_3)$.

5. π-Cyclopentadienyl metal halides, chelates, etc.: e.g., π-$CpTiCl_3$, π-$CpVOCl_2$, π-CpCrBr (acetylacetonate).

All of the compounds in classes 1–4 above are *diamagnetic*, and their formulas can be rather simply classified according to rules very similar to those pertaining to the metal carbonyls themselves (E.15, P.5). As an empirical working rule the metal atom attains the inert gas configuration according to the well-known Langmuir-Sidgwick view. It may be considered that carbon monoxide, the NO^+ ion, and an olefinic bond contribute two electrons, nitric oxide three, and hydrogen, halogens, alkyl groups, etc., one electron. If the $C_5H_5\cdot$ radical contributes five electrons, then, starting with the neutral metal atom, the inert gas rule holds; it may be considered that the $C_5H_5\cdot$radical contributes only one bonding electron (see Section VIII-B) in which case the "fourteen electron rule" holds (E.15). Both these views are merely useful *formalisms* and aids to the prediction of new compounds (cf. P.21) and cannot be regarded as necessarily supporting a particular view of electronic structures (see Section VIII).

B. PREPARATIONS

The types of compound listed above have been made in a great variety of ways. The accompanying reaction schemes (Fig. 6) give some idea of the methods used; references to the preparation of individual compounds are given in Table VIII.

C. STRUCTURAL FEATURES

For the mononuclear species, simple carbonyls, nitrosyl halides, alkyls, etc., the structures are fairly simple, with the π-C_5H_5 group bound to the metal as in, say, ferrocene, with the other ligands or groups on the opposite side of the metal atom, the geometry depend-

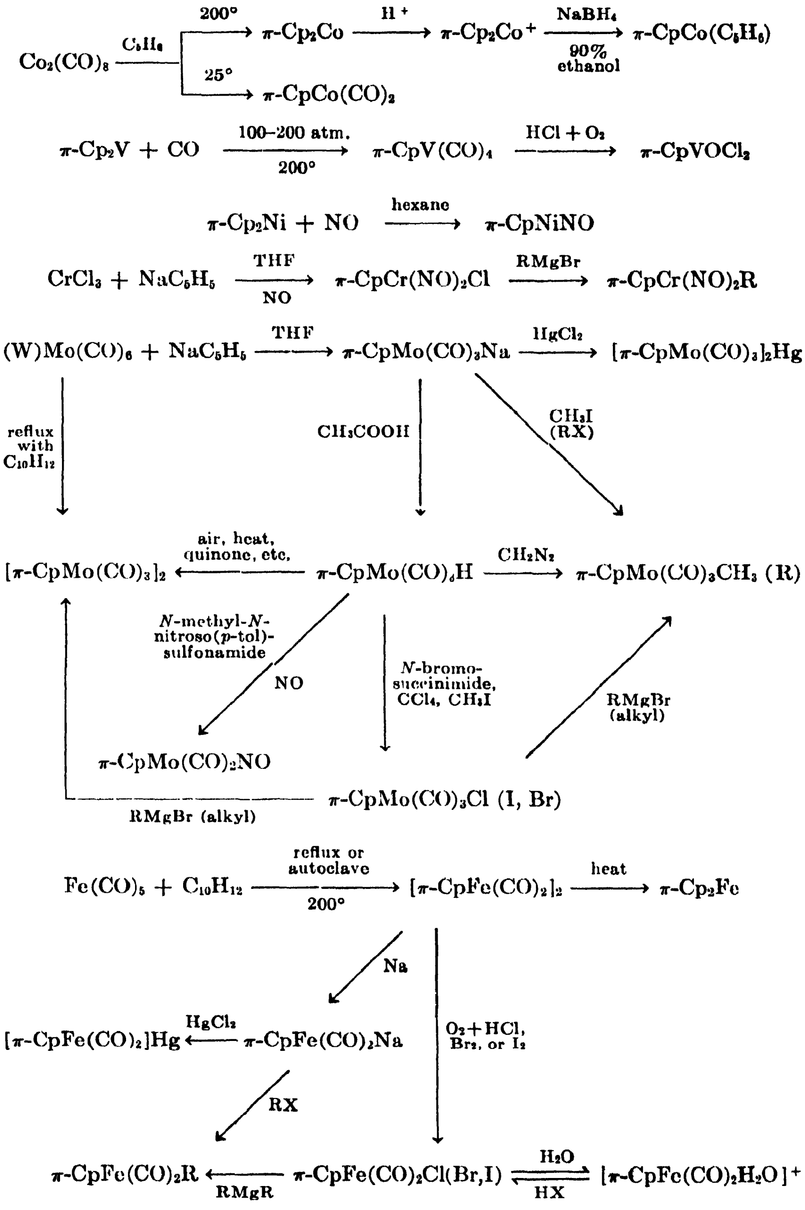

Fig. 6. Some preparations and reactions of mono-π-cyclopentadienyl compounds.

ing, of course, on the formulas (Fig. 7). Infrared studies of many of these compounds have shown that there is a negligible interaction between the π-C_5H_5 group and other ligands, as would indeed be expected if the π-C_5H_5 group were freely rotating about the metal–ring axis as in ferrocene. Accordingly the disposition of the ligands can be ascertained by a consideration of the local symmetry of these groups (E.16,I.8).

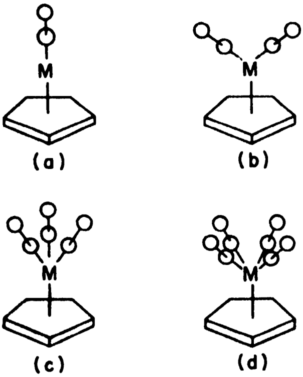

Fig. 7. Structures proposed for some cyclopentadienyl carbonyls and nitrosyls: (*a*) π-CpNiNO; (*b*) π-CpCo(CO)$_2$; (*c*) π-CpMn(CO)$_3$; (*d*) π-CpV(CO)$_4$ (E.15; reproduced by permission).

No X-ray data on a mononuclear π-C_5H_5 species have yet been given, but a private communication from Marsh and Berndt (quoted in G.29) notes that the structure of π-$C_5H_5Mn(CO)_3$ is as indicated in Fig. 7*c*. The infrared evidence is consistent with this structure (E.15,E.16).* It may be noted that in the Group VI metal compounds, π-$C_5H_5M(CO)_3R$, the number of C–O stretching frequencies has been found to depend on the nature of R (F.27). With R = H or CH_3, only two bands are observed, but with R = Cl, Br, and I, three are observed. While this might be interpreted as indicating a different structure with the R group lying along the C_{3v} axis for CH_3 and H, the failure to observe the third C–O band may be due to an overlap of frequencies, particularly since with the halogens the separation decreases with decreasing electronegativity.

The early views on the structure of the binuclear molybdenum and tungsten π-cyclopentadienyl carbonyls (D.4,E.16) have been shown to be incorrect, X-ray studies by Wilson and Shoemaker showing the presence of a metal–metal bond (F.30,G.29). The structure of the molybdenum compound in the crystal is shown in Figure 8.

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* Microwave spectra (J. K. Tyler, A. P. Cox, J. Sheridan, *Nature 183*, 1182 (1959)) also support the proposed structure as a symmetric top.

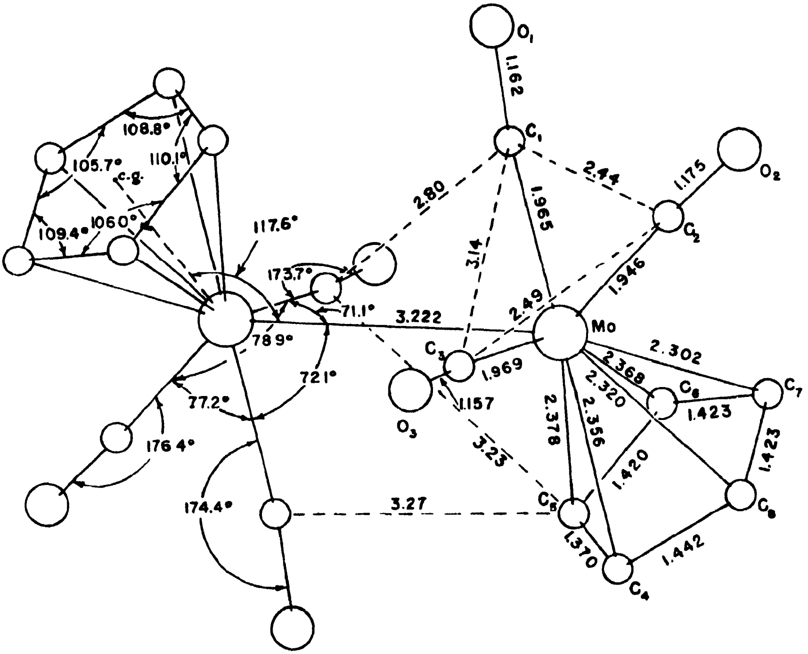


Fig. 8. The structure of $[\pi\text{-CpMo(CO)}_3]_2$ according to Wilson and Schoemaker (G.29; reproduced by permission).

The binuclear iron compound $[\pi\text{-C}_5\text{H}_5\text{Fe(CO)}_2]_2$ appears to be an example of a compound whose structure in the crystal and as the free molecule in solution are not the same. Infrared studies (E.15, E.16) led to the view that there were both nonbridging and bridging carbon monoxide groups present, but that the number of C–O vibrations was not consistent with the presence of a center of symmetry in the molecule. Preliminary X-ray studies (F.30,E.17) indicated that in the crystal the compound did indeed have a center of symmetry. The structure obtained from a more detailed analysis by Mills (I.4) is shown in Figure 9 and a metal–metal bond occurs here also, together with both bridging and nonbridging carbon monoxides. The metal–ring distance of 2.12 A. is longer than that in ferrocene and is comparable to that in di(π-indenyl)iron, and indeed both the last-named and the carbonyl are of lower and comparable stability. However further infrared and Raman measurements (I.5) strongly suggest that in solution the molecule cannot have a center of symmetry in accord with original views.

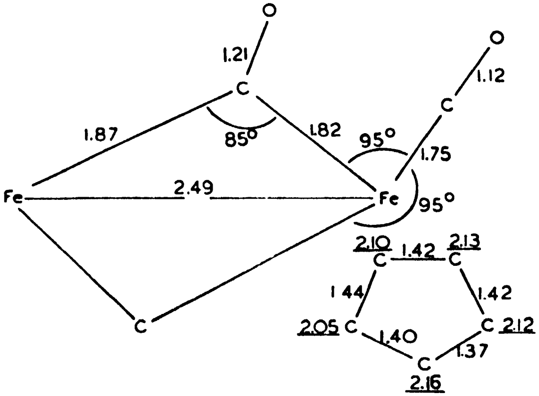


Fig. 9. The structure of $[\pi\text{-CpFe(CO}_2)]_2$ according to Mills (I.4; reproduced by permission).

The microwave spectrum of $\pi\text{-C}_5\text{H}_5\text{NiNO}$ (H.15) has shown a structure the same as that originally proposed (E.15; Fig. 7), the Ni–N–O system being linear with its axis of symmetry normal to the plane of the $\pi\text{-C}_5\text{H}_5$ ring. The computed distance $d_{\text{C–Ni}} = 2.107 \pm 0.001$ A. is somewhat shorter than that in $(\pi\text{-C}_5\text{H}_5)_2\text{Ni}$, and the short $d_{\text{Ni–N}} = 1.676 \pm 0.02$ A. indicates substantial Ni–N multiple bonding as in many other transition metal nitric oxide complexes (J.1).

D. SOME PARTICULAR COMPOUNDS

1. Alkyls and Aryls

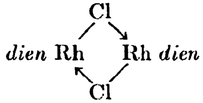
With the exception of the well-known alkyl and aryl compounds of titanium and platinum (J.2) and the di-π-cyclopentadienyltitanium phenyls noted above, the first comprehensive series of transition metal compounds with localized metal–carbon bonds to be made were those derived from π-cyclopentadienyl metal carbonyl and nitrosyl compounds. These alkyls and aryls were made by three methods: (*a*) the reaction of $\pi\text{-C}_5\text{H}_5\text{M(CO)}_3\text{H}$ with diazomethane (F.27,E.21); (*b*) the reaction of the carbonyl or nitrosyl halides with the Grignard reagent (F.27); (*c*) the reaction of the sodium salt of the carbonyl anion with alkyl or aryl halides (F.27; cf. Fig. 6).

Compounds in which a σ-C_5H_5 group takes the place of an alkyl or aryl group have also been prepared (see Section V) by method *b*, and a trimethylsilyl compound, π-$C_5H_5Fe(CO)_2Si(CH_3)_3$, was obtained by method *c* (F.31); undoubtedly many similar derivatives employing other metal or metalloid R groups can be obtained.

The infrared, ultraviolet, and n.m.r. spectra of the alkyls and aryls and unequivocal proof of metal–carbon localized bonds have been given by Piper and Wilkinson (F.27).

2. Olefin Derivatives

From the reaction of rhodium trichloride with cycloocta-1,5-diene, a binuclear halogen-bridged olefin complex



was obtained which on treatment with sodium cyclopentadiene reagent gave a π-cyclopentadienylrhodium cycloocta-1,5-diene complex (Fig. 10; G.30). Considering the two double bonds in the olefin to donate two electrons each, this compound is electronically formally analogous to π-$C_5H_5Co(CO)_2$.

The reduction of the cobalticenium and rhodicenium ions, (π-$C_5H_5)_2M^+$, with sodium borohydride in aqueous ethanol has been found (I.3) to lead to compounds π-$C_5H_5M(C_5H_6)$ in which one π-C_5H_5 ring has been reduced to a cyclopentadiene nucleus. The formulation of these compounds as in Figure 11 was supported by infrared and high resolution n.m.r. studies. On treating the rhodium compound with acid, the rhodicenium ion is partially recovered, but hydrogen and a C_5 olefin are also obtained; the reaction with carbon tetrachloride also gives some hydrogen transfer from the methylene group to form chloroform. It has been shown (I.3) that on reaction of π-Cp_2Co with CH_3I a compound, (π-$C_5H_5)Co(C_5H_5CH_3)$, is obtained.* There is evidence that the methyl group here replaces that methylene hydrogen in (π-$C_5H_5)Co(C_5H_6)$ which is closest to the Co atom.

The reaction of (π-$C_5H_5)_2ReH$ (Section III-E-1) with carbon

* There are similar products from CF_3I, CCl_4, $(CH_3)_3SiCl$, etc. (I.3; cf., also I 40).

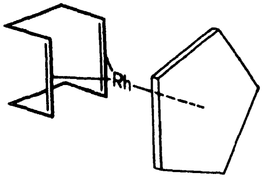


Fig. 10. Presumed structure of the π-cyclopentadienylrhodium-cycloocta-1,5-diene complex.

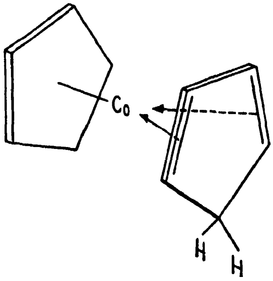


Fig. 11. Proposed structure for π-$C_5H_5Co(C_5H_6)$. No particular relative rotational orientation of the rings is meant to be implied.

monoxide under pressure at ~100°C. leads to a compound of stoichiometry $C_{10}H_{11}Re(CO)_2$; without any experimental foundation, Fischer and Wirzmüller proposed the structure shown in Figure 12*a* in which a σ-C_5H_5 ring (Section V) and a proton (as in π-Cp_2ReH itself) were bound to the metal (G.53). Infrared and nuclear magnetic resonance studies by Green and Wilkinson (I.2) have unequivocally shown, however, that the correct structure for the molecule is one in which a cyclopentadiene group is again bound to the metal, but in contrast to the above cobalt and rhodium derivatives, in this

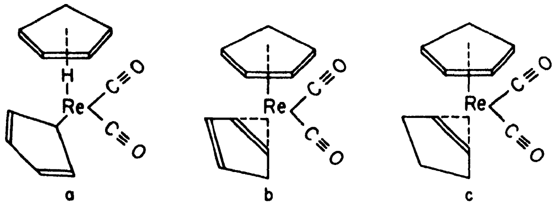


Fig. 12. Possible structures for $C_{10}H_{11}Re(CO_2)$: (*a*) the type suggested by Fischer and Wirzmüller (G.53); (*b*) the type deduced from various experimental data by Green and Wilkinson (I.2); (*c*) structure of the hydrogenation product of (*b*) according to Green and Wilkinson (I.2) (reproduced by permission).

case by only one olefinic–metal link (Fig. 12*b*). This view was further confirmed by catalytic hydrogenation of compound *b* to *c* (Fig. 12) without changing the basic structural features.

3. *Other Derivatives*

The very air-sensitive π-cyclopentadienylchromium acetylacetonate bromide has been referred to above (Section III-D2).

Other compounds, the structures of which are not fully elucidated, are the polymeric nitrosyl sulfide $[\pi\text{-}C_5H_5Mn(NO)S_2]_x$ (F.16) and the incompletely characterized $C_{25}H_{25}Co_2$ (F.2). The reaction of $Ni(CO)_4$ with $\pi\text{-}Cp_2Ni$ has been recently found (H.27) to give the binuclear diamagnetic $(\pi\text{-}CpNiCO)_2$. Iodine on this compound gave a reactive iodide, π-CpNiCOI, and reduction with sodium amalgam gave $Cp_3Ni_3(CO)_2$. Both the bi- and trinuclear compounds were stated to have the C–O stretching frequencies in the bridging region. Structures for the trinuclear compound were suggested, although no evidence for the formulations was obtained.

The stable green oxychloride, $\pi\text{-}C_5H_5VOCl_2$, obtained by the action of air and hydrochloric acid on $\pi\text{-}C_5H_5V(CO)_4$ has recently been described (H.24).

4. *Uses*

The methylcyclopentadienylmanganese tricarbonyl has been claimed in P.21 and P.27 and in various technical publications and bulletins as a successful antiknock agent and additive in hydrocarbon fuels. Although there appears to be no mention of its use in this way, the binuclear carbonyl, $[\pi\text{-}CpFe(CO)_2]_2$, may behave as a catalyst in the hydroformylation process in a way similar to that of cobalt octacarbonyl. This seems reasonable since the hydride, $\pi\text{-}CpFe(CO)_2H$, isolated as a yellow liquid from the reduction of $\pi\text{-}CpFe(CO)_2Cl$ with sodium borohydride (Green and Wilkinson, unpublished work), has reactions comparable to those of $HCo(CO)_4$.

V. σ-Cyclopentadienyl Metal Derivatives

While the cyclopentadienides were known for many years, the first organometallic compounds with a cyclopentadienyl group bound by a localized metal–carbon bond to be characterized were those of silicon (C.3); the unsaturated nature of the products was shown by their formation of adducts with maleic anhydride.

The possibility that a C_5H_5 group could be σ-bonded to a transition metal was first discussed by Wilkinson and Piper in connection with the compounds $C_5H_5CuP(C_2H_5)_3$ (F.21), $(C_5H_5)_2Hg$ (F.21), and

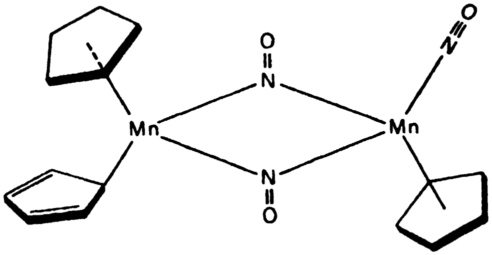


Fig. 13. Structure suggested for $(C_5H_5)_3Mn_2(NO)_3$ by Piper and Wilkinson (F.22). Through a printer's error neither of the structures originally shown in (F.22) is correct. The correct structure, shown above, is given in the erratum (F.22; reproduced by permission).

$(C_5H_5)_3Mn_2(NO)_3$ (F.22). The copper compound was originally prepared (and indeed it was the first transition metal cyclopentadienyl compound to be prepared), although it was assigned an incorrect stoichiometry, by van Peski and Melsen (P.1), through the unusual reaction of cuprous oxide with a mixture of cyclopentadiene and triethylphosphine. Although there was some evidence from spectra and chemical reactions that a σ-C_5H_5 ring was present in all three of the above compounds, and the manganese compound was formulated as shown in Figure 13 with both a σ- and a π-C_5H_5 ring bound to one of the Mn atoms in order to account for infrared spectra and diamagnetism of the compound, the evidence was not unequivocal. Subsequent n.m.r. studies (F.27) of the copper and mercury compounds, along with other compounds noted below, confirmed the presence of a σ-C_5H_5 ring. The situation was developed by the preparation of other compounds containing both σ- and π-C_5H_5 rings. Hallam and Pauson (E.6) reported the compound $C_{10}H_{10}Fe(CO)_2$, which they formulated as a ferrocene nucleus with two additional carbon monoxide groups bound to the metal; such a formulation would, however, be rather difficult to reconcile with the inert gas formalism for the metal atom. Independently, however, this iron compound and the isoelectronic chromium compound, $C_{10}H_{10}Cr(NO)_2$, were made by Piper and Wilkinson (E.7,F.27). Infrared measurements on the compounds showed multiple frequencies in the C–H stretching region in contrast to the single sharp peak in π-C_5H_5 compounds, and also the compounds were shown to react with maleic anhydride; they were accordingly formulated (E.7) as in Figure 14. Later n.m.r. studies by Piper and Wilkinson (F.27) unequivocally showed the presence of two distinct groups of proton resonances, one of these being in the same region as resonances from other π-C_5H_5 compounds. The second resonance, on the low field side relative to the π-C_5H_5 peak, was attributed to protons of the σ-C_5H_5 ring. It is interesting to note that although fine structure might have been expected for a σ-C_5H_5 peak, only one resonance line is observed; the reason for this is still not too clear, although an explanation has been suggested (F.27). This demonstration of σ-bonding in $C_{10}H_{10}Fe(CO)_2$ was subsequently accepted by Pauson and Hallam (F.20) who obtained confirmatory chemical evidence by isolating two isomers with a benzyl residue in either the σ-C_5H_5 or the π-C_5H_5 ring, whereas their original formulation would have allowed only one isomer, and by showing the rapid hydrolysis of the compound with hydrochloric acid.

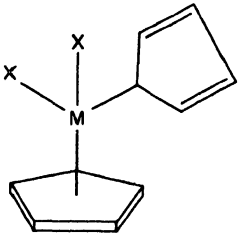


Fig. 14. Structure proposed for $(C_5H_5)_2Fe(CO)_2$ and $(C_5H_5)_2Cr(NO)_2$ by Piper and Wilkinson (F.27).

Compounds considered to have σ-C_5H_5 rings bound to a metal atom are listed in Table IX. Some of these, such as $(\sigma\text{-}C_5H_5)_2Pb$ and $(\sigma\text{-}C_5H_5)_2Sn$, have been found to have dipole moments (Table IV) in accordance with such a structure. However, there has been a brief report (G.2) that the infrared spectra of these lead and tin compounds in solution are very similar to those of ferrocene or nickelocene. This observation would appear to conflict with the above evidence from dipole moments. Infrared measurements of Cp_2Pb and Cp_2Sn (Dave, Evans, and Wilkinson) have confirmed the ferrocene-like spectrum in the NaCl region; n.m.r. measurements give only a single proton peak. The reported dipole moments have also been confirmed by measurements in benzene and in CS_2. The molecules can perhaps be formulated as sandwiches with the rings not parallel.

The compounds $(\sigma\text{-}C_5H_5)_3Bi$, -As, and -Sb have been noted (G.4), but no details are yet available.

TABLE IX

σ-Cyclopentadienyl Compounds

Compound	m.p.	Color	Prep.	IR	UV
Transition metals					
σ-CpCr(NO)$_2\pi$-Cp	66.5–67.2	brown cryst.	F.27	F.27	F.27
σ-CpMn$_2$(NO)$_3$(π-Cp)$_2$	d > 100	purple-black cryst.	F.22	F.22	F.27
σ-CpFe(CO)$_2\pi$-Cp	46	orange-red cryst.	E.6,^{a}F.27, F.20	F.27	F.27,F.20
σ-benzylCpFe(CO)$_2\pi$-Cp	oil	red	F.20	F.20	
σ-CpCuP(Et)$_3$	127–28	white	F.21^{b}	F.21	F.21
Nontransition metals					
σ-CpHgCl(?)		pale yellow	A.4,F.43		
σ-Cp$_2$Hg	83–85d.	pale yellow	F.21^{b}	F.21	F.21
σ-indHgBr	118	colorless	E.3		
σ-Cp$_2$Sn	104–5	white	G.2	G.2	
σ-CpSnϕ_3	130–31	yellow	G.36		
σ-Cp$_2$Snϕ_2	105–6	yellow	G.36		
σ-Cp$_3$Snϕ	64–65	yellow	G.36		
σ-Cp$_3$Sn(?)	71–73	yellow	G.36		
σ-indSnϕ_3	129–30(G.36)	pale yellow	G.36,D.2		
(σ-ind)$_2$Snϕ_2	108–10(G.36) 116–17(D.2)	pale yellow	G.36,D.2		
(σ-ind)$_4$Sn	215	pale-yellow	D.2		
(σ-fluor)Snϕ_3	129–30	colorless	D.2		

(σ-fluor)$_2$Snϕ_2	179	colorless	D.2	
(σ-fluor)$_3$Snϕ	262	colorless	D.2	
(σ-fluor)$_4$Sn	~290	colorless	D.2	
(σ-fluor)Snϕ_2Cl	140–41	colorless	D.2	
(σ-fluor)$_2$SnϕCl	143	colorless	D.2	
σ-(2-dimethylaminofluor)Snϕ_3	151	colorless	D.2	
σ-Cp$_2$Pb	d. ~140	yellow	F.39,G.2	G.2
(σ-fluor)$_2$Pb	238–44	colorless	E.3	
(σ-ind)Pbϕ_3	122	colorless	E.3	
(σ-ind)$_2$Pbϕ_2	107–10	colorless	E.3	
(σ-fluor)Pbϕ_3	118–20	colorless	E.3	
(σ-fluor)Pbϕ_2	138–40	colorless	E.3	
(σ-fluor)Pbϕ_2Cl	160d.	colorless	E.3	
σ-CpIn	sub.	pale yellow	G.7	
σ-Cp$_3$Bi	d.~75	red-orange[c]	G.4	
σ-Cp$_3$Sb(?)		carmine red	G.4	
σ-Cp$_3$As(?)		black	G.4	
σ-CpSiMe$_3$		colorless liq.	C.3	F.21
σ-CpZnEt	66–68	white solid	P.21	
σ-CpZnϕ	?	white solid	P.21[d]	
σ-CpZn *tert*-butyl	?	white solid	P.21[d]	

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[a] Incorrectly formulated.

[b] n.m.r. given, F.27.

[c] Alleged to transform at +20° into black form insol. in organic solvents.

[d] No analysis.

There are a number of σ-bonded derivatives of indene and fluorine which have been made recently; these are listed in Table IX.

VI. Arene Compounds of Transition Metals

A. GENERAL REMARKS

It is now known that the group of organochromium compounds long known as Hein's polyphenylchromium compounds are to be formulated as "sandwich-bonded" arene metal complexes. The early history of Hein's compounds has been reviewed elsewhere (J.2,J.3).

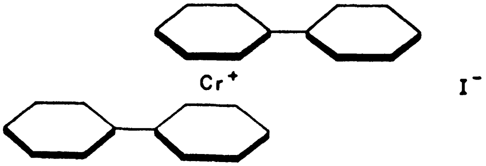

Fig. 15. Sandwich structure proposed for Hein's so-called tetraphenylchromium iodide by Zeiss, Tsutsui, and Onsager (reproduced from Cotton (J.2) by permission.

The renaissance of the studies on "polyphenyl"chromium compounds and their recognition as sandwich-type molecules or ions derived from aromatic hydrocarbons (where the arene nucleus is bound to the metal atom in a manner similar to the bonding in π-cyclopentadienyl metal complexes) is due primarily to the work of Zeiss, Tsutsui, and Herwig. According to Zeiss and Herwig (F.17) and Zeiss and Tsutsui (G.21) the bisarene formulation (Fig. 15) for the "polyphenyl"chromium compounds was due to Lars Onsager. This suggestion was developed by Zeiss and his co-workers and experimental evidence for the arene formulation presented in 1954 and 1955 (E.31,D.23); it has been fully confirmed by subsequent work. In the first major paper (G.21), the essential steps of Hein's method for the preparation of the compounds, i.e., the reaction of phenylmagnesium bromide with anhydrous chromic chloride or chromyl chloride, were reproduced. "Pentaphenyl"chromium iodide and hydroxide, "tetraphenyl"chromium iodide, and "triphenyl"chromium iodide were obtained. The products of reduction of these derivatives with lithium aluminium hydride (and deuteride) were the predicted amounts of benzene and diphenyl. The study also led Zeiss and

TABLE X. Diarene Metal Compounds[a]

Compound	m.p.	Color	Prep.	IR	UV
bz_2V	277–78	red-brown cryst.	G.10		
$[mes]_2V^+$ (as $AlCl_4^-$)		orange	G.10[b]		
bz_2Cr	282–84 [F.17] 284–85 [F.38]	dark brown	F.38,F.17,G.9	E.29	I.13
$bz_2Cr^+{}_{aq}$ and salts and (OH)		orange-yellow	F.38,F.17	G.9[c]	G.13
bz_2CrI		yellow cryst.	F.38,F.17,G.50	G.13	G.13
$(C_6H_5D)_2CrI$		yellow cryst.	G.9	G.9[c]	
$(diphenyl)_2Cr$	~112	dark orange cryst.	F.8		
$(diphenyl)_2Cr^+{}_{aq}$ and salts		orange	F.8,G.9,G.50		
$(diphenyl)_2CrI$	157	orange cryst.	F.8,G.50,G.9	F.8	F.8
bz(diphenyl)Cr	120–21	yellow-brown	G.47		
tol_2Cr[d]					
mes_2Cr[d]					
$hexamethylbz_2Cr$[d]					
bz_2Mo	d. ~115	green cryst.	F.7		
$bz_2Mo^+{}_{aq}$ and salts		brown	F.7		
$[bz_2Re]^+{}_{aq}$ and salts		light yellow	G.11		
$[mes_2Re]^+{}_{aq}$		light yellow	G.11		
Reineckate	d. 120–40	light yellow	G.11		
$[mes_2Fe]^{2+}{}_{aq}$ and salts		orange	F.10		
$[tetralin_2Fe]^{2+}{}_{aq}$		orange	F.10		
$[di(m\text{-}xylene)_2Fe]^{2+}$		orange	F.10		
$[bz_2Ru]^{2+}$(?)		pale yellow	G.49		
$[mes_2Ru]^{2+}$ and salts		v. pale yellow	G.49		
$[mes_2Rh]^{3+}$(?)		brown-red	G.49		

[a] References only since 1954. [b] No analysis. [c] As tetraphenylborate. [d] Mentioned in various notes by E. O. Fischer but no preparative details or properties given.

Tsutsui to suspect the formation in the Grignard reaction of what we now call the dibenzenechromium ion, $(C_6H_6)_2Cr^+$, and this product was indeed later isolated (F.17) by Zeiss and Herwig. The cation was also reduced by hypophosphorous acid to the prototype compound for the arene chromium system, namely, dibenzenechromium, $(C_6H_6)_2Cr$.

Zeiss's early discussions were followed (see note 1 in G.21) by the discovery of a direct preparative route to the arene metal compounds and the independent synthesis of dibenzenechromium by Fischer and Hafner (E.29,F.38). This method involves the direct reaction of the aromatic hydrocarbon with chromic chloride in presence of anhydrous aluminum chloride and aluminum powder at an elevated temperature. The complex is obtained as the tetrachloroaluminate of the arene metal cation; hydrolysis and subsequent reduction with a powerful reducing agent, e.g., sodium dithionite, give the neutral compound (eqs. 10). This so-called "reducing Friedel-Crafts" procedure has

$$6\ C_6H_6 + 3\ CrCl_3 + 2\ Al + AlCl_3 = 3\ (C_6H_6)_2CrAlCl_4$$

$$(C_6H_6)_2Cr^+{}_{aq} \xrightarrow{+e} (C_6H_6)_2Cr \qquad (10)$$

been applied to other arenes and other metals by Fischer and his co-workers. The compounds so far prepared by this and by the Grignard procedure are listed in Table X.

By starting with benzene and diphenyl or diphenyl alone, Fischer and Sues (F.8) were able to make the chromium cations corresponding to Hein's original compounds by the direct method, and by a wide variety of physical methods, e.g., absorption spectra, X-ray edge measurements, etc., were able to show the identity of the compounds with those obtained by Hein's method. In a series of papers (F.9, G.50,F.11,F.42,G.47,G.48) Hein, with his co-workers, has proceeded to re-evaluate the original work on "polyphenyl" compounds, to confirm their stoichiometry and formulation as arene complexes. The products prepared by the Grignard method have been separated by paper (F.11) and alumina column (F.42) chromatography and have been compared with similar products obtained from the appropriate hydrocarbons by the reducing Friedel-Crafts procedure.

B. MECHANISM OF GRIGNARD FORMATION REACTION; TRUE PHENYLCHROMIUM COMPOUNDS

In several papers, Zeiss *et al.* have given particular attention to the mechanism of the formation of arene complexes in the Grignard reaction. Zeiss and Herwig (F.17) obtained the predicted dibenzenechromium ion and reduced it to dibenzenechromium, as noted above. By carbonation and subsequent hydrolysis of the Grignard reaction mixture with both H_2O and D_2O, they were able to obtain some evidence for the existence of both "oxidation-reduction" and "coordination-complexing" steps and postulated intermediate species such as $C_6H_5CrCl_2$ or $(C_6H_5CrCl_2)_2CrCl$. A more detailed later paper (G.9) gave further evidence for the existence of intermediate species.

Further information on the mechanism of the formation of arene complexes in the Grignard reaction, which undoubtedly will make necessary an extensive revision of the ideas noted above, has recently been obtained (G.24). In this note, what appear to be the first *true* simple *phenylchromium compounds* have been described, although it must be noted that the first simple alkyl or aryl chromium species to be demonstrated is the benzyl derivative, $[Cr(H_2O)_5 \cdot CH_2C_6H_5]^{2+}$, which was obtained in solution by reduction of benzyl chloride with a molar solution of chromous perchlorate (G.18), and a π-cyclopentadienylchromium nitrosyl phenyl (Table VIII) was described earlier. The binary phenyl was obtained by Zeiss and Herwig from the Grignard reaction using tetrahydrofuran as solvent; blood-red crystals of two compounds, $(C_6H_5)_3Cr \cdot 3THF$ and $(C_6H_5)_3Cr \cdot 3THF \cdot 3(MgBrCl \cdot THF)$, were obtained. These species were paramagnetic with a moment (3.89 B.M.) corresponding to three unpaired electrons as in Cr^{III}. They were very sensitive to moisture; mercuric chloride was quantitatively converted to C_6H_5HgCl, three moles of the latter being obtained per mole of Cr as $(C_6H_5)_3Cr$. On treating the tetrahydrofuran etherates with diethyl ether, or on heating them to remove tetrahydrofuran, black solids were obtained, which with water gave directly dibenzenechromium together with benzenechromium diphenyl in approximately equal amounts. It was further shown that when the primary products of the Grignard reaction are hydrolyzed under nitrogen, the completely reduced, neutral compounds and *not* the cationic species are obtained.

It is obvious, therefore, that this isolation of a binary phenylchromium, its short lifetime in diethyl ether, and the rearrangement of a phenyl compound to the arene structure in the diarenes will form the basis for a new interpretation of the Grignard preparation.

Independently of this work, Hein (H.22) has also isolated a similar phenylchromium compound, $3C_6H_5Li(C_6H_5)_3Cr \cdot 2.4C_4H_{10}O$, from the reaction of phenyllithium with anhydrous chromic chloride in an ether. This compound is also paramagnetic with three unpaired electrons. Solutions of the compound are also reported to absorb hydrogen under normal conditions to give $(C_6H_5)_3Cr \cdot LiH \cdot 2LiC_6H_5$ (H.22,H.23). The reaction of triphenylaluminum with chromic chloride has been briefly noted as leading to $C_6H_5CrCl_2 \cdot 3THF$ (H.23). The work on $(C_6H_5)_3Cr$ has been carried further by Zeiss and Herwig (H.9) who have found that the reaction of the tetrahydrofuran etherate with 2-butyne gives equal amounts of hexamethylbenzene and 1,2,3,4-tetramethylnaphthalene in a heterogeneous reaction. Homogeneous reactions of the acetylene with either triphenylchromium or triethylchromium in tetrahydrofuran were reported, the alkyl giving only hexamethylbenzene. It was suggested that the formation of hexamethylbenzene requires an intermediate π-complex, such as $R_3Cr(CH_3C{\equiv}CCH_3)_3$, by replacement of the tetrahydrofuran solvent molecules, since the acetylene itself is unaffected by either chromic chloride or the phenyl or ethyl Grignard reagents alone in tetrahydrofuran. The participation of phenylchromium to give the naphthalene by interaction of a phenyl group with two 2-butyne molecules and subsequent *ortho* ring closure opens the way to synthesis of various condensed aromatic ring systems by choosing the appropriate chromium phenyl derivative and acetylene. At the time of writing, progress in this field is rapid.

C. PHYSICAL AND STRUCTURAL STUDIES ON DIARENE METAL COMPOUNDS

1. *Crystal Structures*

The only reported X-ray studies to date are by Weiss and Fischer on dibenzenechromium (Table III), which crystallizes in the cubic system. This work has fully confirmed the sandwich nature of the compound.

2. *Absorption Spectra*

References to infrared and ultraviolet visible absorption spectra are given in Table X. No detailed vibrational analysis of dibenzenechromium is yet available.

The ultraviolet and visible spectra of dibenzenechromium iodide in the crystal and in aqueous and ethanolic solutions have been measured (G.13). The authors claim that the measurements indicate that the electronic states of the benzene rings in $(C_6H_6)_2CrI$ differ greatly from the state in ordinary benzene rings and involve very little aromaticity; they are thus inclined to conclude that the π-electrons of the rings are strongly attracted to the metal. No theoretical treatment of either these or similar spectral measurements on di-π-cyclopentadienyl compounds has yet been attempted and the conclusions so far drawn from the data must be treated with reserve.

3. Nuclear Magnetic Resonance Studies

So far, only a preliminary note on the wide line spectrum of dibenzenechromium has been published (G.33). A rather narrow line was observed at 273°K. of width 3.0 gauss, which was interpreted as indicating motion in the lattice in a manner similar to that in ferrocene which was studied at the same time (see Section III-C-6). The line in bz_2Cr broadened to 12 gauss at 77°K., indicating freezing of motion.

4. Paramagnetic Resonance Studies and Magnetic Measurements

Paramagnetic resonance absorption has been noted in various cationic species, e.g., $[(C_6H_6)_2Cr]^+$, $[(C_6H_5 \cdot C_6H_5)_2Cr]^+$, etc. This word is discussed subsequently (Section VII-A-1) together with magnetic studies.

5. Dipole Moments

The dipole moment of $(C_6H_6)_2Cr$ is zero (Table IV); no studies on other arene metal compounds are reported.

6. Thermochemical Data

The heat of combustion of dibenzenechromium has been determined by standard bomb calorimetric methods (I.9,I.23). The data are given in Table V.

7. X-ray Absorption Edge Studies

Studies on $(C_6H_5 \cdot C_6H_5)_2CrI$ (F.8) are commented on below (Section VIII-A-8).

D. CHEMICAL PROPERTIES

The neutral diarene metal compounds are generally rather reactive compounds. Dibenzenechromium, the most stable of the derivatives, is decomposed by air, being about as sensitive as $(\pi\text{-}C_5H_5)_2Co$, and must be handled in nitrogen or in vacuum. The other neutral compounds (Table X) are both more thermally unstable and chemically reactive. It would appear that the chemistry of diarenes will be nowhere near as broad as that of di-π-cyclopentadienyl metal compounds.

In view of the organic chemistry of ferrocene, attempts to carry out similar reactions with diarene chromium compounds were made using ditoluenechromium, which is more soluble in organic solvents than the rather sparingly soluble dibenzenechromium (G.52). Friedel-Crafts acylation, metallation with butyllithium, mercuration, nitration, etc., were studied, and in all cases the reactions failed to give substitution products; the compound did not react, but decomposed or was oxidized to the ditoluenechromium cation. Exception must be taken to the conclusion (G.52) that these failures indicate that the arene rings in the chromium compound have no aromatic character. The only justified conclusion is that ditoluenechromium and/or any substituted derivatives which may form fail to survive the reaction conditions.

The cationic species—Hein's original cations—have behavior very similar to the π-cyclopentadienyl metal cations, their precipitation reactions being essentially those of the heavier alkalies. The chromium cations are sufficiently stable in aqueous solutions to be handled without difficulty and separated by chromatography, etc.

E. π-CYCLOPENTADIENYL ARENE COMPOUNDS

Considering the electronic structures of ferrocene and dibenzenechromium, we should expect manganese with an odd electron to be able to form a mixed π-cyclopentadienylbenzene compound in which the metal atom is in the +1 oxidation state. Such a derivative, $C_6H_6(\pi\text{-}C_5H_4CH_3)Mn$, has been made by the reaction of C_6H_5MgBr on manganese methylcyclopentadienide and repeated chromatographic separation of the product obtained on hydrolysis from diphenyl (G.23). The compound appears to be of stability intermediate between the diarene chromium and di-π-cyclopentadienyliron compounds.

The mixed iron compound, [π-C_5H_5(mesitylene)Fe]I, was also obtained from the reaction of π-$C_5H_5Fe(CO)_2Cl$ with refluxing mesitylene in presence of anhydrous aluminium chloride (G.23). The compound π-$C_5H_5(C_6H_6)Cr$ has also been made subsequently (H.21). Data are collected in Table XI.

TABLE XI
π-Cyclopentadienyl Arene Metal Compounds

Compound	m.p., °C.	Color	Prep.	IR	UV
bz(π-Cp)Cr	227–29	orange	H.21	H.21	
bz(π-MeCp)Mn	118–18	ruby cryst.	G.23		
mes(π-Cp)FeI		ivory needles	G.23		

F. ARENE METAL CARBONYLS

In strict analogy with the π-cyclopentadienyl metal systems (Section IV) it is possible to have compounds with only one arene group bound to the metal atom together with other ligands. So far only mononuclear arene carbonyls of Cr and Mo have been obtained, but there is no doubt that other types of compound, e.g., nitrosyls, carbonyl halides, etc., as in the case of π-C_5H_5 compounds (Section IV), will be made in due course, the formulas for these being readily predictable by application of the inert gas rule formalism.

The known examples (Table XII) are of the Group VI metals only, and these have been made by Nicholls and Whiting (H.17), Natta *et al.* (H.7), and Fischer *et al.* (H.31) using the direct reaction of the metal carbonyl with the arene derivative at the reflux or under pressure in an autoclave (e.g., eq. 11). Only the simplest of this type of

$$Cr(CO)_6 + C_6H_5NH_2 = C_6H_5NH_2Cr(CO)_3 + 3\,CO \qquad (11)$$

compound, $C_6H_6Cr(CO)_3$, has been made in a different (and much less convenient) manner—by the sealed tube reaction of $(C_6H_6)_2Cr$ and $Cr(CO)_6$ in benzene (G.12).

The carbonyls are all yellow or yellowish in the case of chromium, yellowish green for molybdenum. They all show two strong CO-stretching modes (H.17). This observation is in keeping with local C_{3v} symmetry for the carbonyl groups and since the number of C–O stretches does not depend on the total symmetry of the molecules, free rotation about the metal–arene ring bond may be implied as in the case of the π-cyclopentadienyl derivatives.

TABLE XII
Monoarene Metal Compounds

Compound	m.p.	Color	Prep.	IR	UV
Group VI					
Acetophenone $Cr(CO)_3$	91–92.5	yellow	I.15		
Aniline $Cr(CO)_3$	173–75d. (I.15)	yellow	I.15,H.31,H.17		H.17
	161 (H.31)				
N-Methyl-	127.5–128	yellow	I.15		
N,*N*-Dimethyl-	145.8–46.5	yellow	I.15		H.17
Anisole $Cr(CO)_3$	86–87 (I.15)	yellow	I.15,H.31,H.5		
	84 (H.31)				
Benzene $Cr(CO)_3$	165.5–66.5	yellow	G.12,H.5,H.17, H.31,I.15	H.17	
Acetamino-	134–34.5d	yellow	I.15		
Acetoxy-	94–95.5	yellow	I.15		
Chloro-	102–3 (I.15)	yellow	I.15,H.31,H.5		
	98 (H.31)	yellow			
Fluoro-	122.5–24	yellow	I.15		
tert-Butyl-	83.5–84.5	yellow	I.15		
Hexamethyl-	232 (H.31)	yellow	I.15,H.31		
	211–13d. (I.15)				
Hydroxycarbonyl-	d. 194	orange-red	I.15		
α-Hydroxycarbonylmethyl-	134–35.5		I.15		
Benzoic acid $Cr(CO)_3$	?	orange	I.15,H.31		
Methyl ester	97.5–98.5(I.15)	orange	I.15,H.31		H.17
	95 (H.31)				
Benzyl alcohol $Cr(CO)_3$	95.5–96.5	orange	H.5,I.15		
o-Cresyl methyl ether $Cr(CO)_3$	75–77		I.15		

p-Cresyl methyl ether $Cr(CO)_3$	52–53.5		I.15	
Ethylphenylacetate $Cr(CO)_3$	oil		I.15	
Hydroquinone $Cr(CO)_3$[a]			I.15	
Mesitylene $Cr(CO)_3$	177.5–78(I.15)		H.5,H.17,H.31	H.17
	165 (H.31)		I.15	
Naphthalene $Cr(CO)_3$	d. 150		H.31	
Phenol $Cr(CO)_3$	114		I.15,H.31	
Phenylacetic acid $Cr(CO)_3$	190 d.		H.17,I.15	H.17
Phenylacetate $Cr(CO)_3$	94–95.5		H.17,I.15	H.17
Tetralin $Cr(CO)_3$	116–17.5		I.15,H.5,H.17	H.17
Toluene $Cr(CO)_3$	82.5–83.5	yellow	H.5,H.17,H.31	H.17
o-Toluidine $Cr(CO)_3$	130–31.8	yellow	I.15	
N,*N*-Dimethyl-	76.5–78	yellow	I.15	
m-Toluidine $Cr(CO)_3$	137–38.7	yellow	I.15	
p-Toluidine $Cr(CO)_3$	156–57.5	yellow	I.15	
o-Xylene $Cr(CO)_3$	90–91.4 (I.15)	yellow	H.5,H.31,I.15	
	88–90 (H.31)	yellow		
m-Xylene $Cr(CO)_3$	103–5 (H.31)	yellow	H.5,H.31,I.15	
	107–8.5 (I.15)			
p-Xylene $Cr(CO)_3$	97–98 (H.31)	yellow	H.5,H.31,I.15	
	99–100 (I.15)			
Benzene $Mo(CO)_3$	d. 120–25	greenish yellow	H.31	
Mesitylene $Mo(CO)_3$	d. 130–40 (H.31)	yellow	H.17,H.31,I.15	
	150 d. (I.15)			
Benzene $W(CO)_3$	d. 140–45		H.31	
Mesitylene $W(CO)_3$	160		H.31	
Group VII				
[Mesitylene $Mn(CO)_3$]I		yellow	G.23	

[a] Not obtained pure

In a more detailed study (I.15) it was shown by Nicholls and Whiting that electronic effects in the formation of the arene chromium tricarbonyls from the arene and the carbonyl in diethylene glycol dimethyl ether roughly parallel those observed in nitration studies; the reaction is facilitated by electron-repelling groups on the arene, e.g., NMe_2, and retarded by electron-attracting groups, e.g., —Cl and —$COOCH_3$. Steric factors are also important, the rate in disubstituted benzenes always being $o \sim m > p$; this is held to indicate participation of the aromatic π-electron sextet as a whole in the rate-determining step.

It was also shown that the characteristic properties of functional substituents in the arene chromium carbonyls are largely preserved, e.g., the unstable hydroxylbenzene derivative can be methylated and the aniline complex converted to an acetanilide derivative.

Measurements of the pK_a of benzoic and phenylacetic acid derivatives showed that the —$Cr(CO)_3$ group has a similar electron-withdrawing power to a para-nitro group on an arene nucleus. This observation explains the lack of reactivity of the derivatives toward electrophilic reagents. It may be noted that other $M(CO)_n$ systems, e.g., —$Mn(CO)_3$, will be similarly electron-withdrawing, due to the requirements for multiple bonding in the M–C bond.

Nucleophilic substitution, on the other hand, was much easier in the arene chromium carbonyls than in the parent compounds, e.g. the chlorobenzene compound could be converted into the anisole analog in high yield at 65°.

It was found also that as with the tropylidine metal tricarbonyls (Section VIII), the carbocyclic system could be removed (and recovered) by stronger donors such as pyridine, dimethylphenylarsine, and triphenylphosphine.

VII. Magnetic Properties of Metal Sandwich Compounds

A. GENERAL REMARKS

From the beginning, the magnetic properties have proved to be critical in the evaluation of bonding theories, and considerable data, mostly from bulk magnetic susceptibility measurements, have accumulated. There have been a few electron resonance studies and some measurements of the rate of para-hydrogen conversion. These are discussed below. In Table XIII are reported all data for paramagnetic compounds as well as for some diamagnetic sandwich compounds; many compounds known to be diamagnetic are not listed, although in many cases their susceptibility has been measured. These unlisted compounds are predominantly π-cyclopentadienyl metal carbonyls, arene metal carbonyls, etc. (Tables X and XII); with a very few exceptions (e.g., $C_{15}H_{15}Ni_3(CO)_2$ and azulene$Mo_2(CO)_6$) all such compounds are diamagnetic.

1. *Electron Resonance Studies*

The only compounds so far studied by this technique are π-Cp_2V, manganese cyclopentadienide, and several diarene chromium(I) compounds. The results are discussed below under the respective compounds.

2. *Para-hydrogen Conversion Studies*

It is well known that the conversion of para-hydrogen into the equilibrium mixture of *o,p*-hydrogen is catalyzed by strong magnetic fields, with the rate being proportional to the field strength. Appreciable rates of conversion are attained only in fields of the strength found in the vicinity (on the molecular scale) of paramagnetic ions or molecules.

The rates of para-hydrogen conversion induced by various π-cyclopentadienyl metal compounds in solution have been measured by Schwab *et al.* (D.15,E.30,G.54). No conversion was induced by π-Cp_2Fe, $MgCp_2$, π-Cp_2TiBr_2, π-Cp_2CoClO_4, (π-$C_9H_7)_2Fe$, or (π-$C_9H_7)_2CoClO_4$, and only a negligible rate was observed with π-$CpV(CO)_4$. It was therefore concluded that these substances are diamagnetic in agreement with bulk susceptibility measurements. Using a relation between the specific rate constant for the conversion and the number of unpaired spins per mole, the authors' rate data give for each of the following compounds (E.30) the number of unpaired electrons shown in parentheses: π-Cp_2V (3), π-Cp_2Cr (2), (π-$C_9H_7)_2Co$ (1), π-Cp_2Co (2–3), π-Cp_2Ni (~4), (π-$C_9H_7)_2Ni$ (~1). For the first three compounds the results agree with those obtained from bulk susceptibility measurements; for the last three they certainly do not. For (π-$C_9H_7)_2Ni$ we may note that a magnetic moment of 2.12 B.M. (see Table XIII) has been reported by Fischer. The sample used in

TABLE XIII
Magnetic Data on Cyclopentadienyl and Arene Metal Compounds

Compound	Physical state	Temperature or temp. range, °K.[a]	μ_{eff} (unpaired electrons in parentheses)	Ref.
Group III, lanthanides				
$ScCp_3$	solid	295	dia.	
YCp_3	solid	295	dia.	
$LaCp_3$	solid	295	dia.	
$CeCp_3$	solid	77–295	2.54[b]	
$PrCp_3$	solid	77–295	3.61[b]	
$NdCp_3$	solid	77–295	3.62[b]	F.15
$SmCp_3$	solid	77–295	1.54[b]	
$GdCp_3$	solid	77–295	7.96[b]	
$DyCp_3$	solid	77–295	10.0[b]	
$ErCp_3$	solid	77–295	9.45[b]	
$YbCp_3$	solid	77–295	4.00[b]	
π-Cp_3UCl	solid	77–306	3.16 (2)[c]	F.25
	soln.	305	2.72 (2)	F.25

Group IV				
π-Cp$_2$Ti	solid	77–398	dia.	F.24
	soln.	298	dia.	F.24
π-Cp$_2$Ti·C$_4$H$_8$O				
green	solid	room temp.	para.[d]	F.24
brown	solid	room temp.	dia.	F.24
π-Cp$_2$TiX$_2$[e] (X = F, Cl, Br)	solid	room temp.	dia.	D.11
π-Cp$_2$Ti picrate	solid	298	2.3 (1)	I.11
π-Cp$_2$ZrX$_2$ (X = Cl, Br)	solid	room temp.	dia.	I.11
Group V				
π-Cp$_2$V[e]	solid	78–428	3.82 (3)	F.24
	solid	20–423	3.78 (3)	E.25
	solid	90, 293		D.20
	solid		antiferromag.[b]	H.20
π-Cp$_2$V$^+$	H$_2$O soln.	296	2.86 (2)	D.11
π-Cp$_2$VCl$_2$	solid	296	1.76 (1)	D.11
π-Cp$_2$NbBr$_3$	solid	298	dia.	D.11
π-Cp$_2$TaBr$_3$	solid	298	dia.	D.11
bz$_2$V	solid	88–294	1.73 (1)	G.10,H.32
[mes$_2$V]AlCl$_4$	solid	88–293	2.80 (2)	H.32

(*continued*)

TABLE XIII (*continued*)

Compound	Physical state	Temperature or temp. range, °K.[a]	μ_{eff} (unpaired electrons in parentheses)	Ref
Group VI				
π-Cp_2Cr[e]	solid	298	2.84 (2)	D.4
	solid	90, 295	3 02 ± 0.16 (2)	C.13,E.25
π-Cp_2CrI	solid	90–288	3.81 (3)	F.3
	solid	20–292	3.73 (3)	F.45
bz_2Cr[b]	solid	90, 291	dia.	E.29
	solid	20–288	dia.	F.45
$(CH_3C_6H_5)_2Cr$	solid	90, 292	dia.	F.45
[*sym*-$(CH_3)_3C_6H_3]_2Cr$	solid	90, 292	dia.	F.45
$(C_6H_5{\cdot}C_6H_5)_2Cr$[b]	solid	90, 292	dia.	F.45
(hexamethylbz)$_2$Cr	solid	90, 290	dia.	F.45
$(C_6H_5{\cdot}C_6H_5)bzCr$[b]				
bz_2Cr^+[f]				
as salt of π-$CpCr(CO)_3^-$	solid	90–292	1.73 (1)	F.3,F.45
as tetrachloroaluminate	solid	90–290	1.77 (1)	F.45

$(C_6H_5 \cdot C_6H_5)_2Cr^+$				
as picrate	solid	90, 290	1.80 (1)	F.45
as iodide	solid	90–293	1.75 (1)	F.8
$(C_6H_5)_3Cr(THF)_3$, 3 $(MgBrCl \cdot THF)$	solid	?	3.89 (3)	G.24
$(C_6H_5)_3Cr \cdot 3\ LiC_6H_5 \cdot 2.5\ C_4H_{10}O$	solid	?	3.61 (3)	H.22
$[\pi\text{-}Cp_2MoCl^+][Cr(NH_3)_2(CNS)_4^-]$	solid	room temp.	Cp_2MoCl^+ diamagnetic	D.18
$[\pi\text{-}Cp_2MoCl_2^+]_2[PtCl_6^{2-}]$	solid	room temp.	1.5 (1)	D.18
bz_2Mo	solid	90, 293	dia.	F.7,F.45
bz_2MoI	solid	88–293	1.73 (1)	H.32
azulene $Mo_2(CO)_6$	solid	90–293	~1.5 per atom	I.7
Group VII				
$MnCp_2$[e,f]	solid and soln.	2–496	antiferromagnetic[b]	F.23,G.51,H.20
$Mn(MeCp)_2$	solid and soln.	196–365	anomalous[b]	I.8
$Cp_3Mn_2(NO)_3$	solid and soln.	room temp.	dia.	F.22
$bz(\pi\text{-}MeCp)Mn$	solid	room temp. (?)	dia.	G.23
$[sym\text{-}(Me)_3C_6H_3]Mn(CO)_3I$	solid (?)	room temp. (?)	dia.	G.23
$\pi\text{-}Cp_2ReH$	solid	room temp.	dia.	E.9,I.1
mes_2Re^+ as Reineckate	solid		dia.	H.32

(*continued*)

TABLE XIII (*continued*)

Compound	Physical state	Temperature or temp. range, °K.[a]	μ_{eff} (unpaired electrons in parentheses)	Ref.
Group VIII				
π-Cp_2Fe[e]	solid	298	dia.	B.2
	solid	90, room temp.	dia.	C.13
$(\pi$-$C_9H_7)_2Fe$ [di-π-indenyliron(II)][e]	solid	90, 292, 297	dia.	E.25,C.12,D.6
$(\pi$-$C_9H_{11})_2Fe$ [di-π-tetrahydroindenyliron(II)]	solid	90, 293	dia.	E.25
π-Cp_2Fe^+				
as picrate	solid	298	2.26 (1)	B.2
as $[Cp_2Fe^+][I_{3.25}^-]$	solid	90, room temp.	2.34 (1)	C.13
[*sym*-$(CH_3)_3C_6H_3]_2Fe^{2+}$				
as tetraphenylborate	solid	90, 290	dia.	F.10,F.45
[*sym*-$(CH_3)_3C_6H_3]CpFeI$	solid	room temp.(?)	dia.	G.23
$(\pi$-$C_9H_7)_2Ru$	solid	90, 289	dia.	E.25
$(\pi$-$C_9H_{11})_2Ru$	solid	90, 291	dia.	F.45
[*sym*-$(CH_3)_3C_6H_3]_2Ru^{2+}$				
as $PtCl_6^{2-}$ salt	solid	77, 290	dia.	G.49
π-Cp_2O	?	?	dia.	G.8
π-Cp_2Co[e]	solid	295	1.76 (1)	C.9
	solid	90, room temp.	1.76 ± 0.07 (1)	C.13
π-Cp_2Co^+[e]				
as picrate	solid	298	dia.	B.7
as bromide	solid	90, room temp.	dia.	C.13
as tetraphenylborate	solid	90, room temp.	dia.	C.13

$(\pi\text{-C}_9\text{H}_7)_2\text{Co}$ [di-π-indenyl cobalt(II)]	solid	292	1.76 (1)	C.11
$[(\pi\text{-C}_9\text{H}_7)_2\text{Co}^+]\text{ClO}_4^-$[e]	solid	90, 293	1.76	E.25
	solid	289	dia.	C.11
Cp_5Co_2 (?)	solid	?	dia.	F.2
	soln.	?	para (1)	F.2
$[\pi\text{-Cp}_2\text{Rh}^+]\text{I}_3^-$	solid	298	dia.	C.1
$\pi\text{-Cp}_2\text{Ni}$[e]	solid	77–296	2.88 (2)	D.5
	soln.	298	2.88 (2)	D.5
	solid	291	2.86 (2)	C.8
	solid	—	2.82 (2)	H.20
	solid	90, room temp.	2.86 (2)	C.13
	solid	20–291	2.86 (2)	E.25
$\pi\text{-Cp}_2\text{Ni}^+$				
as picrate	solid	77–295	1.75 (1)	D.5
as tetraphenylborate	solid	90, room temp.	1.82 ± 0.09 (1)	C.13,C.8
$\pi\text{-MeCp}_2\text{Ni}$	solid	82–307	2.9 (2)	I.8
$\text{Cp}_3\text{Ni}_3(\text{CO})_2$	solid	90, 200, 289	1.79 (1)	H.27,H.31
$(\pi\text{-C}_9\text{H}_7)_2\text{Ni}$[g] (?)	solid	90, 291	2.12(?)[g]	E.25

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[a] The temperatures are quoted for measurements made at only one or at only two temperatures. For measurements made at three or more temperatures (so that conformity to the Curie or Curie-Weiss law could be checked) only the range between the lower and upper temperatures is given. Thus such a notation always means that at least one measurement at an intermediate temperature was reported.

[b] See text for further discussion.

[c] Large Weiss constant ($\theta = 138$ degrees).

[d] Not isolated in sufficient quantity to permit quantitative measurement.

[e] Compound also studied by para-hydrogen conversion measurements. See text for a summary of these results.

[f] Also studied by paramagnetic resonance absorption (see text).

[g] The reported moment is difficult to explain except by assuming that the sample measured was impure or partially decomposed. This appears quite possible since the material is very sensitive and unstable (C.11).

the para-hydrogen conversion experiment was supplied by Fischer. Since the compound is very sensitive and unstable the samples may well have been impure. In order to explain the high results for π-Cp_2Co and π-Cp_2Ni (which have 1 and 2 unpaired electrons according to bulk susceptibility measurements; see Table XIII) a rather *ad hoc* and unsupported hypothesis involving the physical remoteness of paired electrons was advanced. Para-hydrogen conversion studies were also made on $MnCp_2$. The results were interpreted to indicate five unpaired electrons in agreement with susceptibility measurements, but it was also suggested that $MnCp_2$ is highly dissociated into Mn^{2+} and Cp^- ions in tetrahydrofuran which is a hypothesis that appears to us neither likely nor necessary. The tetrahydrofuran solution of $MnCp_2$ gives a finite but very low conductivity (F.23).

B. STUDIES ON PARTICULAR COMPOUNDS

1. *Di-π-cyclopentadienylvanadium*

Recently, McConnell, Porterfield, and Robertson (I.13) have studied the paramagnetic resonance of a benzene solution of π-Cp_2V. A g factor of 2.00 and a V^{51} isotropic hyperfine splitting (8 components) equal to 77 mc. were found. At the same time it was observed that π-Cp_2V in benzene is oxidized by air in a few seconds to give a solution which also shows paramagnetic resonance absorption; a g factor of 1.99 was calculated for this species which had hyperfine splittings of about 210 mc. It was suggested that this benzene-soluble paramagnetic species is the π-cyclopentadienyl vanadyl compound π-Cp_2VO, since the intensity contour of the hyperfine splittings is somewhat reminiscent of that for the vanadyl ion in solution.

For π-Cp_2V the small V^{51} hyperfine splitting has been interpreted as indicating that (*a*) in agreement with the suggestion made on the basis of proton resonance studies (H.10), unpaired spin magnetization is spread over the π-cyclopentadienyl rings and (*b*) none of the three unpaired electrons in π-Cp_2V spends more than $\sim 1\%$ of the time in the 4*s* orbital.

The significance of this work is discussed further in Section VIII.

2. *Manganese Cyclopentadienide*

Some preliminary measurements (C.13,D.3) suggesting that this compound has one unpaired electron should be ignored since in both cases specimens of uncertain constitution were studied. Also, at other times (D.21,E.25) measurements now known to be erroneous were reported. The first accurate and extensive study was made by Wilkinson, Birmingham, and Cotton (F.23). In brief summary, it was found that the pure brown-amber rhombic form is antiferromagnetic with a Néel temperature of 134 ± 2°K. Above the Néel temperature some kind of magnetic interactions apparently persist since the susceptibility if still slightly but definitely field-strength dependent and the value of μ_{eff} computed from the Curie-Weiss law in the range 200–420°K. was found to be 7.18 B.M. with a Curie constant C equal to 6.43 and a Weiss constant θ equal to -492°K. At 432°K. (158°C.) a sharp magnetic transition (accompanied by spectral and structural transitions) occurs. The high temperature solid, stable from 432 to 446°K. (m.p.), is pale pink and has a magnetic moment of 5.95 ± 0.05 B.M., indicating five unpaired spins per mole. Above the melting point the Curie law is followed with μ_{eff} equal to 5.86 ± 0.05 B.M. In ether and benzene solutions at room temperature the effective magnetic moment calculated from Curie's law is 5.81 ± 0.10 B.M. Finally it was found that mixed crystals of $MnCp_2$ and $MgCp_2$ sufficiently low in $MnCp_2$ ($< \sim 20$ mole %) had the pink color of the manganous ion and measurements of a sample containing 8.05 mole % $MnCp_2$ showed that Curie's law was followed from 77 to 438°K. with μ_{eff} equal to 5.94 ± 0.05 B.M. From all of these data it was concluded that $Mn(C_5H_5)_2$ contains the Mn^{2+} ion in a ^6S state (5 unpaired electrons) bonded to the rings by essentially electrostatic forces.

These findings of Wilkinson *et al.* (F.23) have recently been fully substantiated. Paramagnetic resonance studies (G.51) have confirmed the antiferromagnetic nature of the rhombic form and ruled out the possibility of covalent bonding at low temperatures since the g factor remains isotropic down to 77°K. A new set of bulk susceptibility measurements over a wide temperature range (from liquid helium temperatures to beyond the melting point) has recently been reported by Leipfinger (H.20). While these results are in qualitative agreement with those of Wilkinson *et al.*, there are quantitative discrepancies. As previously with magnetic measurements from the German workers (E.25), numerical data are unfortunately not given, the results being displayed in a rather small graph. This graph can, however, be read with sufficient accuracy to observe that (*a*) Leipfinger and Wilkinson *et al.* agree on the value of χ_M at the Néel temperature (i.e., at the maxima of their respective curves), although Leipfinger quotes 150 ± 10°K. as the Néel temperature; (*b*) Leipfinger's values above the Néel point are all lower than those of Wilkinson *et al.*, and the slope of his line is different so that he obtains μ_{eff} in this temperature range as 5.69 ± 0.03 and the Weiss constant, θ, as 150° (his numbers); (*c*) Leipfinger's graph indicates that χ_M for the pink, high temperature form is about 9000×10^{-6} c.g.s.u. from which one obtains $2.84(\chi_M T)^{1/2} \approx 5.6$ B.M. as compared with 5.96 B.M. obtained by Wilkinson *et al.* The latter agrees, within experimental error, with the theoretical value of 5.92 B.M. expected if magnetic interactions have been fully cancelled out by the thermal motion and phase changes. There may thus be reason to suspect some systematic error in Leipfinger's values above the Néel point, but we must await a full report of his numerical data and perhaps a referee measurement to be certain of the correct values; it may be noted, however, that the values of Wilkinson *et al.* were obtained on three different susceptibility balances and on many different preparations and the agreement was excellent.

3. Manganese Methylcyclopentadienide

This compound has very anomalous magnetic properties resembling in some ways those of its unsubstituted analog, but with even further peculiarities (I.8). The solid is antiferromagnetic with virtually the same Curie ($C = 6.40$) and Weiss ($\theta = -540°$) constants as manganese cyclopentadienide (F.23). The Néel temperature must be below 196°K. and was not determined. Unlike $MnCp_2$, the methyl derivative has no transition below the melting point. The susceptibility rises abruptly on melting (335°K.) but only to a value corresponding to $\mu_{\text{eff.}} = 4.82$ and rises only to 4.97 at 365°K., suggesting some kind of magnetic interaction in the melt. The liquid can be supercooled and susceptibility values for the supercooled liquid are well below those for the solid at the same temperature. In solution, the compound follows the simple Curie law from 195 to 300°K. with $\mu_{\text{eff}} = 5.83$ B.M., indicating five unpaired electrons for the free molecule as with manganese cyclopentadienide in solution.

4. Di-π-cyclopentadienylvanadium and -nickel at Very Low Temperatures

Leipfinger has studied π-Cp_2V at low temperatures, finding it to exhibit antiferromagnetism with a Néel temperature of ~13.3°K. (H.20). At higher temperatures the Curie law is followed. For π-Cp_2Ni Leipfinger reports a slight deviation from the Curie-Weiss law at temperatures below 20°K.

5. Diarene Chromium Compounds

Paramagnetic resonance absorption has been observed in several of the cationic species (G.26,G.45,G.16). For $(C_6H_6)_2Cr^+$, the American workers find a rather broad peak, the *g* value at the center being 1.983 ± 0.001 (G.45), which is essentially the same as that for the chromic ion, and containing eleven barely resolved hyperfine components (G.26,G.45). It was presumed that two additional components were too weak to be detected. This would make thirteen in all, which could be explained by assuming the level occupied by the unpaired electron to be split by interaction with the nuclear moments of the twelve equivalent hydrogen atoms of the benzene rings. It appears that the spin density on the protons is about twice that in benzene negative ion, $C_6H_6^-$. For the other three compounds, $(C_6H_5D)_2Cr^+$, $(C_6H_6)(C_6H_5 \cdot C_6H_5)Cr^+$, and $(C_6H_5 \cdot C_6H_5)_2Cr^+$ (G.45), *g* values of 1.98 were also observed. In the benzene(diphenyl)-chromium ion resonance, there are twelve hyperfine components and in the bis(diphenyl)chromium ion, eleven components. This suggests that the electron has no appreciable density on the rings not bound to the metal. It may be noted that this evidence for delocalization of "metal ion electrons" onto the rings is complementary to the evidence for the same kind of delocalization in the paramagnetic $(\pi\text{-}C_5H_5)_2M$ compounds, which has been obtained by McConnell from proton resonance experiments (Section III-C-7).

The Russian workers have obtained very similar results (G.16, G.60) and for bz_2CrI, $diphenyl_2CrI$, and $diphenyl_2CrOC_6H_5$ in solution found a *g* value of 1.984 ± 0.001, in excellent agreement with the above value. Hyperfine structure was observed for the last two compounds—at least seven components for $diphenyl_2CrOC_6H_5$—but they did not detect hyperfine structure for the dibenzenechromium ion, presumably because of inadequate resolution; they did, however, show that the band width decreased on substitution of H by D, indicating hyperfine structure to be present although unresolved. These authors also propose delocalization of the unpaired electron to the aromatic rings.

Regarding the bulk susceptibility measurements for compounds of this type, it is to be noted that the so-called "tri-" and "tetraphenyl" chromium compounds which were studied by Klemm and Neuber (A.11) are actually benzene(diphenyl)chromium and bis(diphenyl)-chromium compounds, respectively, and the so-called "pentaphenyl" compound is the phenoxide of bis(diphenyl)chromium. The first true phenylchromium compounds (Section VI-B) have three unpaired electrons.

VIII. The Nature of Bonding in Metal Sandwich Compounds

A. SUMMARY OF CHEMICAL AND PHYSICAL PROPERTIES ESPECIALLY RELATED TO THE BONDING

Before proceeding to discuss the theoretical studies of the nature of the metal–ring bonding, it is pertinent to summarize those aspects of the chemical and physical behavior of the compounds which an adequate bonding theory ought to explain or with which it must be, at least, not inconsistent. These aspects are as follows.

1. The Aromatic Properties of π-Bonded Carbocyclic Rings

While evidence for the aromatic character of ferrocene was provided almost immediately after its discovery (O.0; cf. D.19), the validity of this evidence was denied by Fischer (C.7) for some time, but he has recently acknowledged the aromatic character of these rings (H.4) and has in fact contributed some further evidence. It seems fair to say that the aromatic character of the di-π-cyclopentadienyl metal compounds is an acknowledged fact; indeed ferrocene has been described several times as "superaromatic" by the Russian workers. The evidence for aromatic character is briefly as follows.

(a) Compounds in which aromatic character has been conclusively demonstrated by chemical reactivity are the neutral di-π-cyclopentadienyl compounds, π-Cp_2Fe, π-Cp_2Ru, and π-Cp_2Os, and the cyclopentadienyl carbonyl, π-$CpMn(CO)_3$. Much of the work on ferrocene was reported several years ago and is summarized in other reviews (E.20,G.25). Ferrocene fails to react with maleic anhydride and cannot be hydrogenated in presence of Adam's catalyst (O.0);* it can, however, be cleaved by lithium in ethylenediamine (O.35). Ferrocene undergoes typical aromatic substitution reactions such as Friedel-Crafts acylation (O.0), and reacts with acid anhydrides in presence of hydrogen fluoride (O.8), boron trifluoride (E.20), and stannic chloride (O.1). Ferrocene can be mercurated under very mild conditions (O.1) and metallated readily with *n*-butyllithium (O.1, O.4). It can be sulfonated using acetic anhydride as solvent (O.8) and condensed with aldehydes to yield diferrocenylmethane derivatives (O.8,P.5). The rates of radical polymerization of vinylferrocene and of copolymerization of vinylferrocene with acrylonitrile indicate that ferrocene is even more electron releasing than the phenyl group (O.22b).

Chemical evidence for the aromatic nature of ruthenocene and osmocene has only recently been reported (H.4); both of these compounds undergo Friedel-Crafts acylation with benzoyl and acetyl chlorides and it was stated that mercuration and lithiation reactions had been carried out. The behavior is thus analogous to that of ferrocene. Acetylation of π-CpMn(CO)$_3$ proceeds smoothly to give (π-CH$_3$COC$_5$H$_4$)Mn(CO)$_3$ (I.14,I.32).

It is necessary to recognize that the failure of certain aromatic reactions, such as nitration, sulfonation under ordinary conditions, and others in the case of π-Cp$_2$Fe, -Ru, and -Os, cannot be construed as evidence against aromatic character, since, if the π-Cp$_2$M compound is first oxidized to a cation π-Cp$_2$M$^+$, it is only to be expected that electrophilic reagents will not then attack the positively charged species. Furthermore, the failure of other π-Cp$_2$M compounds, e.g., of Ni, to undergo any typical aromatic reactions is no proof that they lack aromatic character if they are decomposed under the reaction conditions. Both of these facts were first pointed out by the reviewers some years ago (D.19) to refute early denials of aromatic character, and they have also been reiterated subsequently (E.20). Finally, the fact that some (paramagnetic) π-Cp_2M compounds give *some* reaction with maleic anhydride is not evidence of olefinic (i.e., nonaromatic) character unless it can be proved that the reaction is one of addition to a π-C_5H_5 ring *before* it is severed from the metal (F.23), and such proof has never been obtained.

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* Ferrocene was not hydrogenated at 150°/150 atm. with a nickel catalyst (F.2) but has been hydrogenated to cyclopentane and *n*-pentane at 300°/280 atm. (O.19) using nickel catalysts. It may be noted here that π-Cp$_2$Ni forms nickel metal in a very reactive state on hydrogenation. No reports on hydrogenation of other π-Cp$_2$M compounds have been given; in view of the preparation of π-CpCoC$_5$H$_6$, hydrogenation of π-Cp$_2$Co might well give this compound. A report (P.21) merely states that MnCp$_2$ with hydrogen gives "di(cyclopentadienyl) manganese hydride"; but this experiment need not have been made.

The only chemical study of aromatic behavior in an arene metal system was made on ditoluenechromium(0) (G.52). Friedel-Crafts acylation produced *o*- and *p*-methylacetophenones, attempted lithiation gave no reaction, attempted nitration and sulfonation and treatment with dibenzoyl peroxide only oxidized the compound, treatment with diazonium salts produced diphenyl, and treatment with NaH and $NaNH_2$ gave no reaction. The authors concluded that "die ungeladenen Aromaten in den untersuchten neuen Verbindungen vermögen nicht mehr unter Aufrechterhaltung der complexen Metalbindung Substitutions-Reaktionen einzugehen."

(b) It has been pointed out (O.0) that the values of the dissociation constants of ferrocene dicarboxylic acid suggest that the rings are essentially electrically neutral and similar in character to the benzene ring. Quite recently, it has been shown (O.41) that α-hydroxyethylferrocene, like β-phenylethanol, forms an internal hydrogen bond in which apparently the hydroxyl hydrogen seeks the π-electron cloud of the aromatic ring. The strength of the bond appears to be greater for the ferrocene compound than for the phenyl compound, which would suggest greater aromatic character in the former, providing steric differences are not important.

(c) It is well known that the force constants for certain bonds and the frequencies of certain vibrations in classical aromatic compounds such as benzene are characteristic of such compounds. Since there is much chemical evidence for the aromaticity of the rings in ferrocene, it might be expected that the vibrational spectrum would show certain fundamental similarities to that of benzene. This expectation is borne out by the available data. A complete normal coordinate analysis of ferrocene and ruthenocene has been given (H.19) and in addition it has been shown that the valence force symmetry constants for the basic vibrations such as ring deformations, hydrogen stretches, and the parallel and perpendicular hydrogen wagging motions are very much the same in the three systems $C_5H_5^-$ (in ferrocene and ruthenocene), C_6H_6, and $C_7H_7^+$ (F.50). This provides an extremely useful criterion for the aromatic character in other π-cyclopentadienyl metal systems where for one reason or another chemical criteria are not obtainable or are of questionable significance. Perusal of the infrared spectra of π-cyclopentadienyl metal compounds which have appeared in the literature (complete references are found in Tables II, VIII, and IX) will reveal that they are all quite similar in the principal assignable regions of absorption, such as C–H stretching, ring deformation, and hydrogen deformation. This would certainly seem to constitute *prima facie* evidence that the aromatic character and the nature of the metal–ring bonding is roughly the same in all of them whether or not they can all be made to undergo any one or set of several reactions. No rigorous studies, comparable to those on π-cyclopentadienyl, of the vibrational spectra of arene metal compounds, from which some indication of the nature of the bonding might be gleaned, have as yet been published. In view of the fact that aromatic character in classical aromatic systems such as benzene is attributed to a high density of polarizable electronic charge above and below the plane of the carbocyclic system, it would appear that in π-cyclopentadienyl metal systems there exists a similar mobile and polarizable electron cloud above and around the rings. Certain of the experiments noted above indicate this in a rather direct way. Thus it would appear that a substantial π-electron density is retained by the rings after the formation of the sandwich bond to the metal, and a satisfactory bonding theory ought to lead naturally to such an expectation.

2. Internal Rotation of the Rings

There is now considerable evidence that π-bonded cyclopentadienyl rings are free to rotate about the axis from the metal atom to the center of the ring with a very low if not zero hindrance. Important evidence on this point is as follows.

(a) No rotational isomers of di-π-cyclopentadienyl compounds with at least one substituent on each ring have been isolated. Further, measurements of dipole moments of several ferrocene derivatives bearing substituents on both rings (Table IV) have suggested that either (*1*) free or only slightly hindered rotation if the rings relative to one another is taking place in the molecule, or (*2*) if the rotation does not actually occur in the molecule once formed, some process involved in the synthesis must have led to an essentially statistical distribution of the product molecules among all possible rotational isomers. This latter possibility does not seem likely and has not been suggested as a preferable conclusion to (*1*) by any workers so far. The early chemical evidence for free rotation has been presented by Pauson (E.20), and recently Struchkov has considered the stereochemistry of ferrocene and its derivatives in some detail (G.56). Rosenblum and Woodward have recently published a comprehensive account of evidence for rotation in ferrocene derivatives (O.72).

(b) From the diffuseness of the lines in an electron diffraction study of ferrocene (E.14) it was suggested that, at least above 400°C., essentially free internal rotation takes place.

(c) It is well known that in the crystal ferrocene has a staggered (D_{5d}) structure. This does not of course mean that hindered rotation does not occur (see below) but only that the staggered form is the form of minimum potential energy and over a period of time, the molecule will most often be found in this configuration. It is therefore significant that ruthenocene has recently been found to exist in the eclipsed (D_{5h}) configuration (G.44); dibenzenechromium also exists in an eclipsed configuration in the crystal (F.38). This seems to indicate (*1*) that the configuration is determined mainly by lattice forces or (*2*) that the configuration in $(\pi\text{-}C_5H_5)_2Fe$ is determined by small van der Waals' forces which become insignificant when the rings are further apart as they are in $(\pi\text{-}C_5H_5)Ru$ or (*3*) a combination of these two factors. What these results would appear to contradict clearly is the idea that the metal–ring bonding itself, presumably the same in essential features in both compounds, imposes any stereospecificity on the rotational configuration.

(d) Proton resonance studies of crystalline ferrocene and dibenzenechromium (Sections III-C-6 and VI-C-3) down to low temperatures show that line widths are quite narrow, indicating considerable rotational motion with low activation energy. Unfortunately, with $\pi\text{-}Cp_2Fe$ and other molecules having essentially cylindrical shapes and low moments of inertia, it is not possible, as yet, to say whether the line narrowing is due to internal motion, i.e., rotation, or to rotation of the whole molecule in the lattice, or to a combination of both.

Recently, however, proton resonance studies of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ (I.10), in which rotation of the molecule as a whole seems rather unlikely, have shown that rotation of the rings relative to the $[Mo(CO)_3]_2$ portion of the molecule occurs down to at least 77°K. and that the energy of activation for this process cannot exceed a few kilocalories. The activation energy may well be much less than this and further work at lower temperatures should provide more information.

(e) As noted previously in the π-cyclopentadienyl metal carbonyls and related compounds, the number of other ligand, notably carbon monoxide, frequencies in the infrared is independent of the total symmetry of the molecules and is consistent with very small interactions between the other ligands and the π-cyclopentadienyl or substituted π-cyclopentadienyl ring.

In summary, it appears quite certain that rotation of π-bonded cyclopentadienyl rings about the metal–ring axis of symmetry is at the most only slightly hindered and that this may be due only to van der Waals' or lattice forces. Thus any acceptable bonding theory must not restrict the rotational orientation of the ring, but must allow of free or very nearly free internal rotation.*

3. Magnetic Data

All of the magnetic data so far reported have already been summarized and discussed. It certainly seems reasonable to demand that any bonding theory which is sound should be able to make correct predictions of the number of unpaired electrons in the various sandwich molecules and ions. It must, of course, be recognized that success in this respect is not alone a warranty that the order of energy levels is correct, as will be seen in Section VIII-B.

4. Ultraviolet and Visible Spectral Data

Such data are as yet fragmentary (Tables II and X). It is not simple to say just how much one can demand of a theory in this respect. It is quite possible that a theory with serious defects could give a meretriciously good account of the few available spectral data—indeed this, as will be seen, seems to have occurred. Conversely, a theory might be quite useful and generally valid and yet fail to be particularly accurate in predicting the spectrum, since to do so it must fix the positions of excited states quite accurately and moreover the observed bands must be reliably assigned. Thus while an extremely accurate and detailed theoretical treatment would account for the spectra, no treatment could be fairly rejected for failing this test alone.

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* Of course, as discussed in detail by Struchkov (G.56), bulky substituents can hinder rotation and joining the rings together by a carbon chain will also prevent motion other than oscillation about a most favored position.

Regarding the assignments of ultraviolet spectra, studies of the dichroism of ferrocene (D.14,E.5) and dibenzenechromium iodide (G.13) have been reported and should in due course be useful in this respect.

5. Thermochemical Data

Only for $(\pi\text{-}C_5H_5)_2Fe$ and -Ni and for $(C_6H_6)_2Cr$ are heats of formation known (Table V). These do not provide a particularly sensitive test of theoretical energy level schemes, since in no case can they be obtained from the theory except by introducing many, necessarily rough, estimates of level separations in the ring π-orbitals and in metal promotional energies and relative ionization potentials. Any treatment from which the heats of formation are obtainable within ±50% is probably satisfactory on this account.

6. Fragments Produced in Electron Bombardment

As has been noted above (Section III-C-4), studies of such fragments by mass spectrometry have shown that there are characteristic differences in the relative amounts of various fragments obtained from the covalent di-π-cyclopentadienyl metal compounds as compared to the ionic dicyclopentadienides. Also the appearance potentials for various fragments from $MnCp_2$ and $MgCp_2$ and the π-Cp_2M compounds of the first transition series (M = V, Cr, Fe, Co, Ni) have been reported. In view of the many uncertainties in deriving bond energy values from the appearance potentials (some of which are intrinsically uncertain due to "tailing" difficulties), it is difficult to say how faithfully one can expect theory to account for the observed results. At any rate no attempt at correlation has yet been made.

7. Evidence of Electron Delocalization

Shifts of proton resonance peaks in various paramagnetic $(\pi\text{-}C_5H_5)_2M$ compounds (Section III-C-6) and electron resonance studies on $(\text{arene})_2M^+$ species (Section VII-C-4) lead to the conclusion that so-called metal ion electrons are appreciably delocalized onto the rings in several cases. The approximate extent of such delocalization and perhaps its quantitative variation from one compound to another should be deducible from a satisfactory bonding theory.

8. X-ray Absorption Edge Fine Structure

Recently the X-ray absorption edges of a number of π-cyclopentadienyl metal compounds (E.2,F.46,G.58,I.11) and diarene chromium compounds (F.8,G.57) have been studied.

Absorption peaks constituting fine structure on K edges are believed to correspond to electronic transitions in which 1*s* (*K*) electrons are excited to the lowest available (unfilled) orbitals in increasing order of energies and culminating finally in complete ionization of the metal atom (J.5). If it is assumed that the *g*-*u* selection rule is applicable, then only transitions to *p* and *f* orbitals will have high intensity and consequently the location and occupancy of such orbitals can be inferred from the edge structure. Even in rather simple cases, however, unambiguous interpretation can be difficult (J.6–J.9), and while German workers have given very simple interpretations for a host of complexes (F.46,G.57,G.58) these may be questioned (J.8). The German workers have expressed the opinion that the observed edges for π-cyclopentadienyl metal compounds indicate the complete filling of the 4*p* orbitals (E.2,F.46,F.33). This conclusion is not necessarily correct since it is reached by ignoring the presence of antibonding orbitals. This matter can best be treated in detail after the theoretical work on metal–ring bonding has been discussed below.

B. THEORETICAL TREATMENTS OF SANDWICH BONDING

1. Di-π-cyclopentadienyl Metal Compounds

The unusual structure and extraordinary stability of ferrocene immediately aroused great interest in the nature of the bonding in this and analogous compounds. Due to the complexity of the problem, no truly quantitative treatment is possible, although several treatments which involve numerical computations will be referred to as quantitative in contrast to those which are of a purely qualitative if not intuitive nature. Because of the impossibility of performing a truly quantitative calculation, discussions of the bonding have involved considerable clash of opinion. In what follows, we have tried to summarize the various contributions and to evaluate them critically.

The best presently available test of any view of the bonding is how well it accords with the facts set out in the previous section, but again the relative importance and exact interpretation of the various facts are in themselves matters in which some latitude of opinion legitimately exists. Of far more value than any of these presently available data, however, would be extensive measurements on the electronic spectra and *a fortiori* electron resonance spectra for the paramagnetic species. Such data, which are practically nonexistent at the time of writing,* will doubtless accumulate in the future and should provide extremely sensitive criteria for judging the validity of theories. It would indeed not be surprising if much of the present theory, since it is really very crude, were found to be unsatisfactory in all but its broadest features.

At the outset, when the sandwich structure for ferrocene was proposed (B.2,B.10), it was also proposed by both groups (and by others (C.15)), that the iron atom attains an inert gas configuration by accepting all of the π-electrons from both rings into its vacant $3d$, $4s$, and $4p$ orbitals. The German workers (B.10,B.11) amplified this idea with the more specific proposal that the bonding in ferrocene could be considered to resemble in great detail that classically postulated in the so-called penetration complexes of Fe^{II}, e.g., $[Fe(CN)_6]^{4-}$. Thus they suggested that the three electron pairs in a cyclopentadienyl ion, $C_5H_5^-$, be considered as standing at the corners of an equilateral triangle, while the Fe^{II} ion orbitals were occupied so as to provide for the existence of an empty set of d^2sp^3 hybrid orbitals. The six electron pairs of the two $C_5H_5^-$ anions were than assumed to be completely transferred to the six empty metal ion orbitals, thus producing an inert gas configuration. This theory was severely criticized (D.19) on the grounds that it failed to accord with the aromatic nature of ferrocene, that it would lead to an incorrect magnetic moment for $(\pi\text{-}C_5H_5)_2Ni$, that the attainment of an inert gas configuration could scarcely be a *sine qua non* for stability, since compounds such as $(\pi\text{-}C_5H_5)_2Ti^{2+}$ were stable, and finally because the symmetry of the sandwich structure is not that required for the use of *octahedral* d^2sp^3 orbitals. It was also noted that the assumption by Fischer that in $(\pi\text{-}C_5H_5)_2Ni$ the two electrons in excess of the number in ferrocene would occupy 4*d* orbitals rather than some lower orbital where they would perforce be paired, was completely *ad hoc.** Nevertheless, far from abandoning this view, Fischer has recently stated (F.33) his belief that "die *Gesamtheit* (italics in the original) aller Ring-π-elektronen . . . in die zentralen Metalle mit einbezogen ist," and characterized his view of the bonding as requiring the "*Einbeziehung aller π-Elektronen*" (italics in the original) into the metal atom. In the meantime, however, much effort had gone into developing more sophisticated theories of the bonding within the framework of molecular orbital theory.

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* Vacuum ultraviolet, ultraviolet, visible, and near infrared spectra of π-Cp_2V, -Cr, -Fe, -Co, and -Ni, $MnCp_2$, $MgCp_2$, and NaCp are available (I.12).

Jaffé's Work. The first molecular orbital treatment was that of Jaffé (C.4). His work indicated the various types of MO's which could be important in the bonding and led quite naturally to the conclusion that free internal rotation should be possible. The latter conclusion has been confirmed experimentally, as noted previously, and has been verified theoretically by all subsequent MO treatments. Jaffé also made estimates of the relative energies of the various MO's** and suggested that eight electron pairs might be principally involved in metal-ring bonding, although no quantiative support was given for this statement. Jaffé also suggested an interpretation of the ultraviolet spectrum of ferrocene. Extension of Jaffé's treatment to predict the magnetic properties of the $(\pi\text{-}C_5H_5)_2M$ compounds of the other metals of the first transition series by simply adding or subtracting the appropriate number of electrons is not wholly successful; but of course Jaffé, unlike later workers, did not have the advantage of hindsight in this respect, since the other molecules had not been prepared at the time of his studies.

Dunitz and Orgel (Treatment I). The point of departure for most of the subsequent work was provided by Dunitz and Orgel (C.6), who pointed out the symmetry properties of the various ring and metal orbitals in the D_{5d} symmetry of the molecule.*** This classification is important since it is only orbitals of the same symmetry type which can have any net overlap. For the metal atom, the orbitals of interest are of the following symmetry types: A_{1g} (d_{z^2}; s), A_{1u} (p_z), E_{1u} (p_x, p_y), E_{1g} (d_{xz}, d_{yz}), E_{2g} (d_{xy}, $d_{x^2-y^2}$). Each individual ring has D_{5h} symmetry and possesses π-molecular orbitals of symmetry types A_1, E_1, and E_2. When the two rings are considered together in the relative orientation which they have in the molecule (which has a symmetry center), these may be combined into even (g) and odd (u) pairs, viz., A_{1g}, A_{1u}, E_{1g}, E_{1u}, E_{2g}, E_{2u}.

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* Later, essentially these same criticisms were reiterated by Schwab and Voitländer (E.30).

** Jaffé incorrectly used C_{5v} symmetry, which, while detracting somewhat from the clarity of the discussion, does not in itself introduce any fundamental errors.

*** We may remark that for the molecule in the eclipsed configuration (cf $(\pi\text{-}C_5H_5)_2Ru$) the point group symmetry is D_{5h}. However, the groups D_{5h} and D_{5h} are isomorphous, and while the notation for the various orbitals will be altered, the treatment will not be otherwise affected by using D_{5h} symmetry.

Dunitz and Orgel then discussed the molecular orbitals formed by combining the metal and ring orbitals classified in the manner just described. They suggested that the occupation of the atomic orbitals of iron is $(A_{1g})^2(E_{2g})^4(E_{1g})^2$, (where the $3d_z{}^2$ A_{1g} orbital is meant, and the 4s orbital is not explicitly considered). The ring system was assumed to have the electron configuration $(A_{1g})^2(A_{1u})^2(E_{1u})^4(E_{1g})^2$-$(E_{2u})^0(E_{2g})^0$. The order of filling of the ring orbitals was estimated from simple LCAO theory which gives an energy order $A < E_1 < E_2$. Dunitz and Orgel then pointed out that overlap of the half-filled E_{1g} orbitals of the metal atom and the ring system would lead to the formation of two "covalent-ionic" bonds and also suggested that there would be some tendency for metal E_{2g} electrons to spread into the vacant E_{2g} orbitals in the rings.*

While the above treatment contains the essence of later and more detailed work, it does in fact fail to predict unambiguously the diamagnetism of ferrocene if one considers the 4s orbital (which has been ignored) to be approximately degenerate with, or perhaps a little more stable than, the 3d orbitals (D.5). Moreover, it leads to the conclusion that $(\pi\text{-}C_5H_5)_2Ni$ should be diamagnetic (D.5), whereas that compound has two unpaired electrons. Dunitz and Orgel's prediction that manganese should form a ferrocene-like compound, since it has sufficient orbitals of appropriate symmetry, has, of course, not been fulfilled.

Moffitt's Treatment. Following the note by Dunitz and Orgel, the MO approach was extended by Moffitt (D.9). It may be noted parenthetically that Moffitt's paper gives an excellent elementary account of the principles underlying the use of symmetry arguments in this sort of problem, and also gives some illuminating drawings of the orbitals concerned.

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* Similar, essentially qualitative, arguments were also given by Craig *et al.* (D.13).

Moffitt's work extends that of Dunitz and Orgel in two main ways: (*1*) the relative energies of the metal and ring orbitals are estimated, (*2*) it is recognized that the two A_{1g} metal orbitals ($3d_{z^2}$ and $4s$) can mix and that the electrostatic effect of the rings will tend to increase the stability of that mixture [$(4s) \sin \alpha - (3d_{z^2}) \cos \alpha$], which concentrates electron density in the equatorial plane of the molecule between the rings, and decrease the stability of the orthogonal linear combination [$(4s) \sin \alpha + (3d_{z^2}) \cos \alpha$], which concentrates electron density just in the region of the rings. The results of Moffitt's treatment are shown in the energy level diagram for ferrocene in Figure 16. It can be seen that the mixing and splitting of the metal A_{1g} orbitals, the stable combination being denoted ha_g and the unstable combination ka_g, leads to a completely unambiguous prediction of diamagnetism for ferrocene. Also, if it is assumed that the ka_g orbital is approximately degenerate with the $4p$ orbitals, as indicated in Figure 16, then the triplet ground state of $(\pi\text{-}C_5H_5)_2Ni$ is explained. The triplet state of $(\pi\text{-}C_5H_5)_2Cr$ is also accounted for. However, $(\pi\text{-}C_5H_5)_2V$ has three rather than one unpaired electrons and it is necessary here to assume that the ha_g orbital has dropped only a little relative to the (unfavorable) energy of spin-spin interaction, so that the electrons remain in separate orbitals with parallel spins. The diamagnetism of $\pi\text{-}Cp_2Ti$ could also be accounted for.

Moffitt's treatment was still of a rather qualitative nature and left several important questions unanswered. For example, some interactions between the ring A_{1g}, A_{1u}, E_{1u}, and E_{2g} orbitals and orbitals of the same symmetries on the metal are allowed by symmetry. Moffitt averred that such "secondary" bonding forces were probably much less important than the E_{1g}–E_{1g} interaction, but ventured no quantitative estimate. It may also be noted that while Moffitt's energy level scheme does indeed explain the paramagnetism of $(\pi\text{-}C_5H_5)_2Ni$, this is by no means the only way to do so.* More quantitative work along the lines laid down by Dunitz and Orgel and by Moffitt was carried out by Dunitz and Orgel (E.13) (hereafter DO.II), Yamazaki (F.18), Liehr and Ballhausen (G.3) and Ruch

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* A treatment encompassing many of the essential features of Dunitz and Orgel's treatment (I) and Moffitt's work was later rendered in German (E.30)

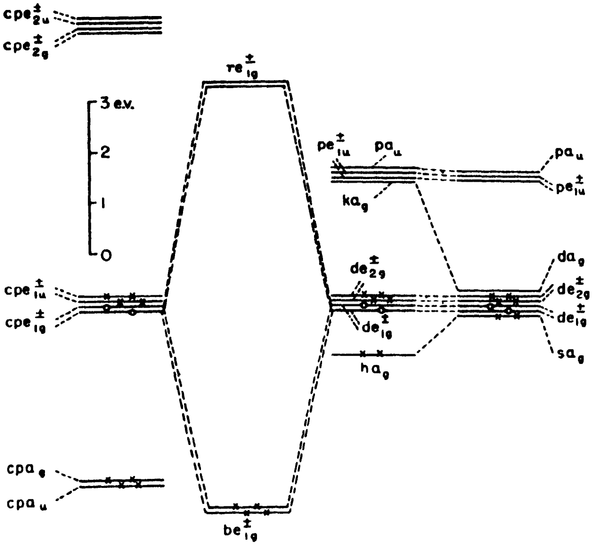

Fig 16. Molecular orbital energy level diagram of ferrocene according to Moffit (D.9; reproduced by permission).

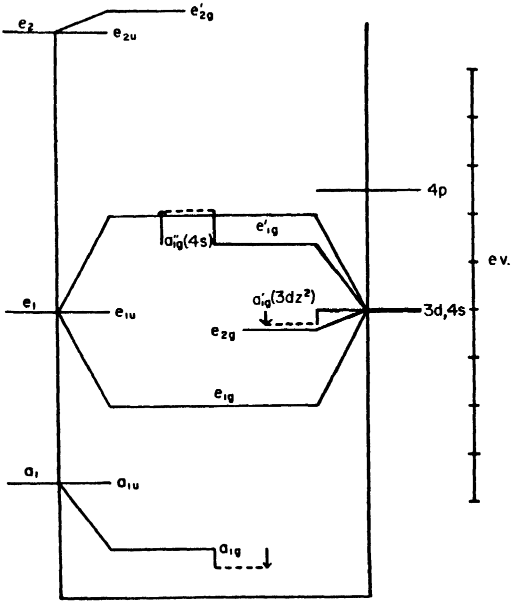

Fig. 17. Molecular orbital energy level diagram of ferrocene according to Dunitz and Orgel (E.13; reproduced by permission).

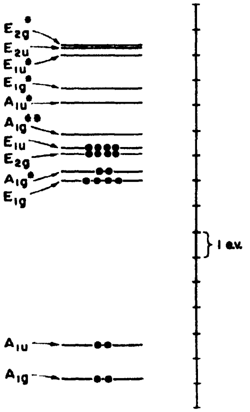

Fig. 18. Molecular orbital energy level diagram of ferrocene acerding to Yamazaki (F.18). Drawn by the authors from Yamazaki's numerical results.

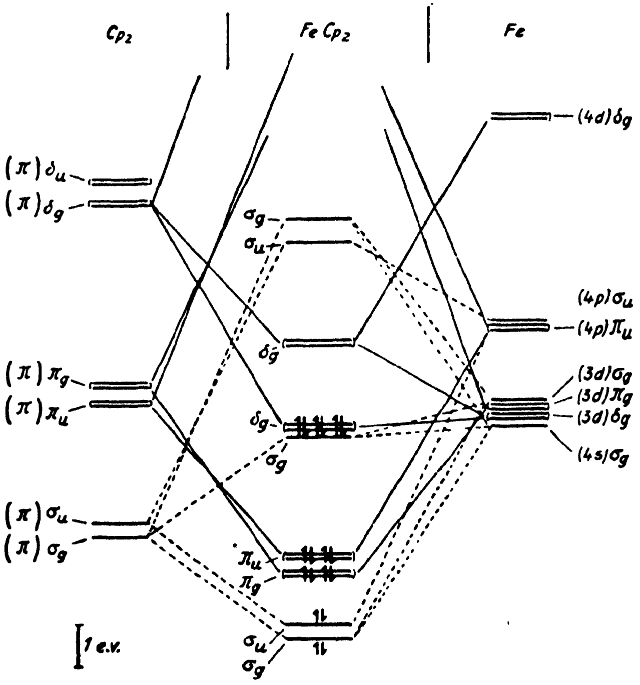

Fig. 19. Molecular orbital energy level diagram of ferrocene according to Ruch (F.34; reproduced by permission).

(F.34). It will be convenient to discuss these papers in the order mentioned.

Dunitz and Orgel, Treatment II. In DO.II, an attempt was made to provide a more quantitative idea of the relative importance of the various possible bonding interactions in ferrocene. The major premises in this work were the following: (*1*) It was assumed, following Moffitt, that the iron $3d$ and $4s$ orbitals were all approximately degenerate and further that they lie at essentially the same energy as the e_1 π-MO's of the rings. (*2*) The relative separations of the a, e_1, and e_2 ring orbitals were calculated from simple LCAO theory, taking the usual exchange integral, β, to be 60 kcal. per mole, with an approximate correction for overlap. (*3*) It was assumed that matrix elements for all interactions are proportional to overlap integrals using Slater atomic orbitals. (*4*) While the value of α (one of the radial parameters in Slater MO's) was taken as 1.6 for carbon (as given by Slater's rules), the α's for the iron $4s$ and $3d$ orbitals were also set equal to 1.6 and not to the Slater values. While there is some basis for abandoning the strict Slater rules (D.13), the choice of 1.6 is somewhat arbitrary and these authors themselves point out that "the numerical overlap integrals in this range are quite sensitive to the choice of α," and that if $\alpha = 2$ is used, "the changes which occur are quite significant." They also completely neglect the iron $4p$ orbitals on the grounds that it is difficult to assign α values to them and to allow for their low electron affinity. (*5*) Finally, it was assumed that the e_{1g}–e_{1g} interaction could be taken as 2.0 volts per electron.

The results of the calculations are expressed in the energy level diagram (Fig. 17) reproduced from DO.II. The exact positions of a''_{1g} relative to e'_{1g} and of a'_{1g} relative to e_{2g} could not be estimated with certainty. It is, of course, just these details which determine the ability of the theory to account for the magnetic data. If we accept the statement made in DO.II that this energy level diagram should be adequate for all the other neutral di-π-cyclopentadienyl metal compounds, although there will be slight shifts of the metal orbital energies with respect to the fixed energy level scheme of the ring system, then the magnetic properties of the $(\pi\text{-}C_5H_5)_2M$ compounds for M = Ti, V, Cr, Fe Co, and Ni can be accounted for by the following prescription of the order and population of levels:

πCp$_2$Ti $(a_{1g})^2(a_{1u})^2(e_{1g})^4(e_{1u})^4(a'_{1g})^2$
π-Cp$_2$V $(a_{1g})^2(a_{1u})^2(e_{1g})^4(e_{1u})^4(e_{2g})^2(a'_{1g})^1$
or $(-)^{12}(a'_{1g})^1(e_{2g})^2$, assuming a'_{1g} and e_{2g} to be degenerate or nearly so.
π-Cp$_2$Cr $(a_{1g})^2(a_{1u})^4(e_{1g})^4(e_{1u})^4(a'_{1g})^2(e_{2g})^2$
π-Cp$_2$Fe $(a_{1g})^2(a_{1u})^2(e_{1g})^4(e_{1u})^4(a'_{1g})^2(e_{2g})^4$
or $(—)^{12}(e_{2g})^4(a'_{1g})^2$
π-Cp$_2$Co $(a_{1g})^2(a_{1u})^2(e_{1g})^4(e_{1u})^4(a'_{1g} + e_{2g})^6(a''_{1g})^1$
or $(—)^{18}(e'_{1g})^1$
π-Cp$_2$Ni $(a_{1g})^2(a_{1u})^2(e_{1g})^4(e_{1u})^4(a_{1g} + e_{2g})^6(e'_{1g})^2$

The following points are worthy of notice. The major differences between the energy level schemes of DO.II and Moffitt lie (*1*) in placing the e'_{1g} (antibonding) orbitals below the metal $4p$ orbitals, and (*2*) in attributing most of the upward shift of the a''_{1g} orbital to interaction with the ring a_{1g} orbital and not to the $4s$–$3d_{z^2}$ interaction as in Moffitt's treatment. However, the amount of *ad hoc* placing of levels (in this case of the a'_{1g} relative to e_{2g} and a_{1g} relative to e'_{1g}) is still as great as is required in Moffitt's treatment if all of the magnetic data are to be accounted for.

With the above-mentioned assumption that the e_{1g}–e_{1g} bonding interaction energy is about 2 volts per electron (or 8 volts for the *four* e_{1g} electrons), stabilization of 2.8 volts due to a_{1g} interactions and 1.6 volts due to e_{2g} interactions were calculated. Thus altogether the bonding energy of ferrocene from appropriate valence states of 2$C_5H_5\cdot$ and Fe(0) was calculated to be 12.4 e.v. It was shown that an energy of this magnitude can be reconciled with the known heats of formation of (π-$C_5H_5)_2$Fe and (π-$C_5H_5)_2$Ni using reasonable assumptions as to the valence states of the metal atoms. Thus according to DO.II, while the e_{1g}–e_{1g} overlap makes the dominant contribution to the bonding a_{1g}–a_{1g} and e_{2g}–e_{2g} interactions are not negligible. While they did not attempt a quantitative estimate of the e_u–e_u interaction, they state that they believe that it too will be significant.

Yamazaki's Work. Yamazaki (F.18) has reported the results of a calculation for ferrocene similar in principle to that of DO.II. Certain of his premises are somewhat different, however. In particular, the following points may be noted. (*1*) α for the carbon $2p$ orbitals is taken as 1.6 but for the iron orbitals he takes $\alpha_{3d} = 2.20$ and $\alpha_{4s} = \alpha_{4p} = 0.878$. (*2*) β is taken as ~55 kcal. per mole. (*3*) Matrix elements are again assumed proportional to overlaps of Slater orbitals. Yamazaki's work is reported in a very brief manner making it impossible to see directly what kind of ordering of levels in the combined metal and ring systems is implied. Also, the levels are labelled according to D_{5h} symmetry. In Figure 18 we have drawn the molecular energy levels obtained by Yamazaki, relabelling in terms of D_{5d} symmetry. It may be seen that this level scheme is considerably at variance with that of DO.II in many quantitative respects and, more important, differs in certain qualitative respects, particularly in the relative placement of the A_{1g}^*, A_{1u}^*, and E_{1g}^* levels. Unless we assume that something fairly drastic happens in going from $(\pi\text{-}C_5H_5)_2Fe$ to $(\pi\text{-}C_5H_5)_2Ni$, so that both the nondegenerate levels go above the E_{1g}^* level, we shall arrive at the incorrect prediction of diamagnetism in $(\pi\text{-}C_5H_5)_2Ni$. While Yamazaki's work is more complete in the sense that he has included more interactions, it may well be less reliable if his choice of α values for the iron atom is incorrect. They differ enormously from the choices of DO.II. Yamazaki also claims that his treatment gives a reasonable account of the ultraviolet spectrum of ferrocene, but this may well be fortuitous. A more detailed paper is to be greatly desired.

Liehr and Ballhausen's Treatment. Liehr and Ballhausen (G.3) have given a quantitative treatment which differs from those of DO.II and Yamazaki in the manner of computing interaction energies. They use a method related to the electrostatic formalism of the ligand field theory and their computations extend to all of the $(\pi\text{-}C_5H_5)_2M$ compounds of the first transition series. In addition to the basic approximation involved in their method of estimating matrix elements, there are several other approximations or assumptions worth noting. (*1*) They follow Moffitt in assuming that interactions of ring and metal orbitals other than the e_{1g}–e_{1g} interaction are comparatively small and they neglect them. (*2*) Assumptions are made as to the effective nuclear charges for the *s* and *d* orbitals of the various metal atoms. These are made in a reasonable and consistent, but somewhat *ad hoc*, way in order to obtain certain agreement with the known magnetic properties of the compounds. (*3*) It is assumed that the ring and metal e_{1g} orbitals are equi-energic in all of the compounds discussed. While Moffitt has stated this to be the case for ferrocene, it is doubtful if it is so for all of the other metals, especially Ti and V. However, exactly the same assumption (or at least the assumption that the difference is never very large) is made by Dunitz and Orgel in attempting to account for the magnetic properties of the compounds of the other elements of the first transition series by extension of their results for ferrocene.

Ruch's Treatment. Ruch (F.34,F.48,D.16) has presented the energy level diagram for ferrocene which is shown in Figure 19, which he implies is based on computations of overlap integrals. It will be noted that his notation differs from that used by other workers because Ruch begins by ignoring the five-fold symmetry of the rings and treating them instead as discs. Thus his notation is that appropriate to the point group $D_{\infty h}$. However, the groups D_{5d} and D_{5h} are closely related to $D_{\infty h}$ and this approximation with respect to symmetry is in itself quite inconsequential so far as the reliability of the numerical results is concerned. For the convenience of the reader we may note that Ruch's symbols correspond to those for D_{5d} symmetry in the following way:

$\sigma \rightarrow A_1$; $\pi \rightarrow E_1$; $\delta \rightarrow E_2$; g and u have the same meanings.

Ruch does not state all of his assumptions and approximations as explicitly as others have done. It appears by comparison of Figures 17 and 19 that his estimates of the separations of the π-MO's of the rings and of the $(3d4s)$–$4p$ separation are about the same as those of DO.II. There is considerable uncertainty about a number of vital points, however. While his estimate of the energy of the $4d$ orbitals is not unreasonable, he himself makes no attempt to justify it. He is quite vague about how the reported overlap integrals were obtained, stating only that the self-consistent field orbitals of Manning and Goldberg (J.4) were used for iron. Thus one can only wonder what sort of orbitals Ruch used for the rings and for the iron $4p$ and $4d$ levels, since the work of Manning and Goldberg does not extend to these. Moreover, his energy level scheme has quite a few bizarre features. It is difficult to see, for example, why the antibonding π_g-MO is shown to be at least 8 e.v. above the energy of the combining orbitals while the bonding π_g-MO is only 3 e.v. below. To a fair approximation one would expect the two energies to be about equal. Finally, Ruch does not state what, if any, relationship he has assumed between his overlap integrals and the energies shown in Figure 19.

In view of these considerations, one can scarcely escape the conclusion that Ruch's treatment is not in fact quantitative (or at the very least, let us say that he gives no good reason for us to suppose that it is) but rather that it is quite arbitrary in many important respects and cannot be accepted on the same footing with the work described above.

The Use of Approximate Symmetries. There has been a certain amount of discussion about the use of approximate symmetries rather than the exact (D_{5d}) symmetry in treating ferrocene and related molecules. Cotton and Wilkinson first objected to the "octahedral" view of the bonding on the ground, *inter alia*, that the symmetry of the required metal orbitals was not in conformity with the symmetry of the sandwich molecules (D.19), and this objection has been reiterated by others (E.30,F.49). Subsequently Ruch (F.34) has admitted that the d^2sp^3 set of hybrid orbitals which he uses is not the well-known set appropriate for a truly octahedral system such as $Cr(CO)_6$ or $[Fe(CN)_6]^{4-}$. In the latter case it is the d_{xy} and $d_{x^2-y^2}$ orbitals which are used, whereas Ruch uses the d_{xz} and d_{yz} orbitals. Thus his d^2sp^3 set has the symmetry of a trigonal antiprism (D_{3d})* but is not essentially dissimilar to the octahedral d^2sp^3 set. Further, Linnett (F.35) has pointed out that by starting with orbitals rigorously appropriate to D_{5d} symmetry, linear combinations may be formed to give a new set of equivalent orbitals of D_{3d} symmetry.** Thus it has been made quite clear that Ruch's orbitals are related to the usual octahedral orbitals and further that they can be transformed into symmetry orbitals of group D_{5d} without altering the energies obtained from the secular equations (F.35). Thus the symmetry question is not crucial. The important question and the true root of controversy concerns the extent to which electron density is transferred from the rings to the metal atom via dative bonding, and further, whether there is significant dative bonding in the opposite sense as well. It is more or less a matter of indifference how the various orbitals concerned are labelled or hybridized.

Electron Distribution. The question of the distribution of electron density in ferrocene may be posed by referring to Figures 16, 17, and

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* Voitländer (F.49) has stated that a set of D_{3d} orbitals cannot be made using d^2sp^3, but only using d^3p^3 hybridization. This is incorrect. Five of the required orbitals are d_{xy}, d_{yz}, p_x, p_y, and p_z. The sixth orbital may be either an s orbital (which Ruch has used) or a d_{z^2} orbital, since both are of the same symmetry type in the D_{3d} group.

** These are not actually equivalent orbitals in the Lennard-Jones sense (H.6), as Linnett seems to imply, but that is not a matter of any real importance.

19. There is no disagreement about the fact that the e_{1g}–e_{1g} overlap is very extensive and that the electrons in the e_{1g} bonding orbital are about equally shared between the iron atom and the rings to form essentially homopolar bonds. Thus this source of bonding does not materially affect the distribution of electron density between the iron atom and the rings. From Figure 17 it can be seen that the other possible overlaps, which are all between filled and empty orbitals so that transfer of electron density must result, are the following, where the arrows indicate the direction of electron transfer:

$$\begin{aligned} &Cp\ a_{1g} \rightarrow 4s \\ &Cp\ a_{1u} \rightarrow 4p_z \\ &Cp\ e_{1u} \rightarrow (4p_x, 4p_y) \\ &Cp\ e_{2g} \leftarrow (d_{xy}, d_{x^2-y^2}) \end{aligned}$$

The two extreme views are (*a*) that all of these forms of dative bonding are negligible compared to the e_{1g}–e_{1g} interaction and (*b*) that the first three of these forms of dative bonding listed are very extensive, with the last one perhaps also extensive. The first view is that taken by Moffitt and by Liehr and Ballhausen and has been in the past favored by the American group of chemists. The second view is that of the inert gas structure proponents, notably Fischer and Ruch, *viz.*, that altogether five electrons (i.e., "die Gesamtheit aller Ring π-elektronen") from each ring are incorporated into the metal atom. The current status of the theoretical work justifies, we believe, the following statements:

1. There is no question that one *can* regard the metal as using a set of six orbitals of *roughly* the octahedral type if one so desires (*vide supra*). The important point is whether complete transfer, or something close to that, of π-electrons into the metal orbitals is a tenable view in the light of experimental facts and recent theoretical work.

2. While all of the so-called quantitative work on the bonding in ferrocene is obviously very crude, still it is the best that is available contemporarily and cannot be ignored. Taking the results of DO.II as the best guide in the matter, it appears that while the e_{1g}–e_{1g} interaction does provide the greater part of the metal–ring bonding, other interactions are not negligible. On this basis, the first view must therefore be regarded as too extreme. The evidence for aromatic character and, in general, the retention of considerable π-electron

density in the rings can be reconciled with interactions of the relative magnitudes proposed by DO.II. It must be remembered that two orbitals, one an empty metal orbital and the other an occupied ring orbital, can interact to produce a small but useful contribution to the metal–ring bonding without there necessarily being a great deal of drift of electrons to the metal atom. To put it another way, consider the interaction of the a_{1g} orbitals. It is probable that the bonding a_{1g} orbital is largely a ring orbital, so that while the interaction with a_{1g} metal orbitals makes a contribution to metal–ring bonding, the lowest a_{1g} orbital is at the same time still important in carbon–carbon π-bonding. A similar situation may exist for the a_{1u} and the e_{1u} interactions, while at the same time the e_{2g} interaction has a tendency to return electron density to the rings. Since, however, the ring e_{2g} orbitals are antibonding with respect to the rings themselves, the drift of e_{2g} electrons to the rings cannot be considered simply as an antidote to loss of electrons from orbitals which are bonding with respect to the ring system, and the idea of compensation cannot be pushed very far.

3. The Langmuir-Sidgwick concept of metal atoms attaining an "inert gas configuration" is venerable but unfortunately crude and vague; it is at the best only a formalism. If we take it to mean only that the metal atom will, where possible, utilize (to *some*, but not necessarily a *great*, extent) all of the lower-lying orbitals which eventually become filled in the succeeding inert gas atom, then it is a useful qualitative guide to chemical facts as noted in a previous section. That it cannot be taken literally—i.e., in the sense that all such low-lying orbitals participate *on an equal footing* and *equally* with ligand orbitals in σ-bond formation—should be obvious. For example, quite the opposite *formalism, viz.*, assuming the *absence* of any covalent bonding which uses metal orbitals, is embodied in the simple ligand field theory which has had striking success in correlating the chemical behavior and properties of transition metal complexes. It seems to us that the statements of Fischer, such as those quoted previously, tend to convey the rather literal idea of the "inert gas configuration" given first above. If this be so, then it appears that Fischer's views are also too extreme, but in the opposite direction from those frequently expressed by the American group.

4. Thus, the soundest view at the present time seems to be that all low-lying metal orbitals make some contribution to the bonding

with their relative contributions varying somewhat from one (π-$C_5H_5)_2M$ compound to another, so that it is a crude oversimplification to ignore all but the e_{1g}–e_{1g} interaction. At the same time, it is also a crude oversimplification to suppose that all metal orbitals and all ring orbitals contribute strongly and equally to the bonding, since the available calculations do not support this, nor can one then account for the aromatic character of the compounds.

Interpretation of X-ray Absorption Edges. Having reviewed the status of bonding theories for (π-$C_5H_5)_2M$ compounds, we may briefly discuss the interpretation of X-ray absorption edges of such compounds. The German workers (E.2,F.46,F.33,G.57,G.58) have proposed that the main absorption peaks be assigned to $1s \rightarrow 5p$ transitions, while the small bumps about 5 volts lower on the leading edge of the main peaks be assigned to $1s \rightarrow 4p$ transitions. From the relative weakness of the latter they conclude that the metal $4p$ orbitals are almost fully occupied. While this interpretation could conceivably be correct, it is presumptuous to assume that it is. Firstly, if the "$4p$" orbitals referred to in the "$1s \rightarrow 4p$" transition are nearly filled, then they are presumably bonding orbitals. There must then be somewhere a related set of antibonding orbitals also having appreciable $4p$ character (probably even more $4p$ character since the $4p$ orbitals are initially the highest energy orbitals of a_{1u} and e_{1u} symmetry in the system), which are empty. Where, then, is the peak corresponding to a transition to these? In all probability, whether the $4p$ orbitals are strongly or negligibly involved in the bonding, the strong peak at $\sim$20 volts represents a transition to them. The very weak bumps cannot be assigned with any confidence. Perusal of the extensive data available (leading references were given in Section VIII-A-8) on the K edges of numerous complexes, not only cyclopentadienyl or arene metal compounds, will reveal many cases in which there are weak low energy absorptions obviously not due to $1s$–$4p$ transitions. It is doubtful if the $\Delta l = \pm 1$ selection rule is strictly applicable in covalent complexes and thus very weak absorptions at energies below the first main peak are susceptible of various interpretations.

2. Mono-π-cyclopentadienyl Metal Compounds

The chemical and physical properties of these compounds suggest that the metal–ring bonding is similar, in general, to that in the

(π-$C_5H_5)_2M$ compounds, and the bonding has often been referred to as "sandwich bonding" (E.15,F.26) to indicate this presumed similarity. In view of this, the molecular orbital treatments of the bonding in ferrocene can be carried over in essentials, although the lower symmetry and greater diversity of orbitals (considering those of NO, CO, etc.) make the situation somewhat more cumbersome. Orgel (F.26) has outlined a qualitative treatment for π-CpNiNO, π-CpCo-$(CO)_2$, π-CpMn$(CO)_3$, and π-CpV$(CO)_4$ assuming the structures proposed by Piper, Cotton, and Wilkinson (E.15) to be correct, as has since been shown to be true for π-CpNiNO (H.15) and π-CpMn-$(CO)_3$.* Piper *et al.* in proposing structures for these compounds prior (1954) to the appearance of the quantitative work on the bonding in ferrocene, took the view outlined in the only substantial theoretical discussion then available, that by Moffitt, that four of the ring electrons were retained mainly in the ring, so that "effectively" the outer electron shell of the *metal atom* has nearer fourteen than eighteen electrons. However, they stated quite clearly that "on the basis of the proposed structures it is formally possible that there is some contribution to the bonding from all three 4*p* orbitals," but since they are some 3 e.v. higher than the 4*s* and 3*d* orbitals and "since it is only *necessary* to use, on the average, one of these in constructing the hybrids, no further promotion of the metal atom *need* be invoked and it may be supposed that the remaining components of the 4*p* band are left unoccupied." Orgel, writing after some quantitative calculations were available for guidance (F.26), guessed that the involvement of the 4*p* levels was a good deal more extensive. However, there is no difference between his conclusions and those of Piper *et al.* except in the *degree* to which some of the e_1 and a_1 electrons of the ring are supposed to participate in metal–ring bonding. That there are altogether eighteen electrons present is not a remarkable observation and does not, obviously, permit one to conclude that all of them are bonding electrons in the specific sense of "metal-to-ring bonding" electrons. It is worth noting that there may well be more involvement of ring e_1 and a_1 electrons than was supposed by Piper *et al.*, but Orgel's view is basically conjecture although the manner of its presentation tended to obscure this fact. The demonstration (I.14,I.32) of aromatic behavior of π-CpMn$(CO)_3$ in the Friedel-

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* R. Marsh (California Institute of Technology), private communication to F. A. Cotton.

Crafts reaction and the isolation of the acyl-substituted derivatives certainly indicates considerable residual electron density in the π-C_5H_5 ring, however.

3. Tri-π-cyclopentadienyl Metal Compounds

While the rare earth compounds of stoichiometry $C_{15}H_{15}M$ have been shown (F.15) to have ionic properties and are best considered as tricyclopentadienides, the compound $C_{15}H_{15}UCl$ has been shown (F.25) to contain the cation $(\pi\text{-}C_5H_5)_3U^+$, in which the metal–ring bonding is substantially covalent. The first molecular orbital account of this bonding was that of Moffitt (in F.25). He considered the filled a π-MO's of the rings to be too stable to contribute effectively to the bonding, and the empty e_2 levels to be too high in energy to be of great importance, and directed attention to the e_1 orbitals. Linear combinations of these, from the three rings, are of symmetry types a'_2, a''_2, e', and e'' in the point group D_{3h} which is appropriate if the effects of relative rotational orientation of the rings are ignored. It was then shown that only by making use of the 5f orbitals of uranium can bonding orbitals of the necessary symmetry types be obtained. On this basis, the bonding is attributed mainly to three electron pair bonds similar to the e_{1g}–e_{1g} bonds in, say, ferrocene.

A valence-bond theory involving more extensive overlap of ring and metal orbitals has also been put forward (G.55). In this work the 5f orbitals of uranium are also used in combination with 6d, 7s, and 7p orbitals to produce nine σ-bond orbitals. These may be described as three equivalent sets. In each set there are three orbitals trigonally directed and the three 3-fold axes (one for each set) lie in a plane making angles of 120 degrees with each other. The six π-electrons of a given ring then overlap with the three hybrid orbitals of a given set. Clearly, just as Moffitt's treatment is simply an adaptation of his treatment of the di-π-cyclopentadienyl metal compounds, so is the Russian treatment akin to the octahedral theory which has been proposed for these compounds. In view of what has been said above concerning the bonding in $(\pi\text{-}C_5H_5)_2M$ compounds, both of these views may be considered as limits, with the actual state of affairs lying somewhere between them. Further, concerning the orbitals involved, it may be noted that "in the heaviest atoms, where there are so many electrons at comparable distances from the nucleus, the simple language which has been devised to account for bonding between light atoms is no longer applicable, and there are several, alternative, equally compelling, descriptions which can be employed," utilizing either $5f$, the almost as favorable $6f$, and/or also $6p$ orbitals (J.10).

4. Cyclopentadienides

Compounds of a predominantly ionic nature have been referred to as cyclopentadienides. It must, of course, be recognized that here, as in most other areas of inorganic chemistry, such distinctions must not be taken perfectly literally. For a purely ionic $M(C_5H_5)_2$ compound, one would expect the same sandwich configuration, as a result of electrostatic forces (F.23,H.6), as is found in a highly covalent compound such as ferrocene, and indeed this configuration is found in $Mg(C_5H_5)_2$ and $Mn(C_5H_5)_2$, both of which are regarded as cyclopentadienides. Further, the configuration of TlC_5H_5 (H.6) is apparently the same as that in, say, π-$C_5H_5Mn(CO)_3$, while the former appears to be essentially ionic and the latter highly covalent. Finally, it is assumed that the structures of the $M(C_5H_5)_3$ compounds of the lanthanides, Sc and Y, which are essentially ionic, are the same as that of $(\pi\text{-}C_5H_5)_3U^+$, which, as the written formula implies, is predominantly covalent. It must be assumed in all cases that there is some ionic and some covalent character, but that in any particular compound one or the other usually predominates. In ferrocene apparently, due to the availability of de_{1g} orbitals (and to a smaller extent, others) of the proper energy, the bonding is essentially homopolar—that is, covalent. It may well be that in the titanium and vanadium compounds the higher energy of the $3d$ orbitals makes the bonding more ionic (G.34) and indeed there is some experimental evidence for this (F.23). In $Mg(C_5H_5)_2$ and TlC_5H_5, where there are no d orbitals of low energy available, the bonding is essentially ionic. However, it is probably not completely so, since some covalent interaction of metal p orbitals and ring e_1 orbitals can occur (H.6). Again in the tricyclopentadienides of the lanthanides, some covalent contribution of the sort which dominates in $(\pi\text{-}C_5H_5)_3U^+$ doubtless could occur since it is permitted by the assumed geometry of the molecules, but it appears to be negligible for the same reason that the lanthanides generally do not form complexes with much covalent character—their high electropositivity and the fact that the $4f$ orbitals are well buried.

While in general the existence of ionic compounds appears to correlate with the electropositive character of the metal, in the case of $Mn(C_5H_5)_2$ an additional factor seems to be important—namely, the well-known reluctance of Mn^{II} to use its $3d$ orbitals in covalent bond formation which in turn is attributed to the great stability of the $3d^5$ (^6S) configuration. Again, of course, some covalent contribution due to ring e_{1u} and metal e_{1u} (p_x, p_y) overlap is possible (H.6), but while a quantitative estimate is difficult, this is probably small. Since the ferricenium ion $(\pi\text{-}C_5H_5)_2Fe^+$, which is isoelectronic with $Mn(C_5H_5)_2$, is clearly sandwich-bonded, the energy difference between ionic and sandwich bonding may not be too large but it is nevertheless critical.

5. Arene Metal Compounds

No attempt has as yet been made to treat the bonding in such compounds, e.g., dibenzenechromium, in a quantitative way. Fischer and co-workers adopt the view that all twelve π-electrons are drained from the benzene ring into metal orbitals, similar to the π-cyclopentadienyl case. Liehr and Ballhausen have noted that quantitative calculations could be made by a simple extension of their method (G.3). We may also note that calculations similar to those of Dunitz and Orgel and of Yamazaki could also be made. The only important differences in the two ring systems, C_6H_6 and C_5H_5, are (*1*) the ionization potentials of the two will not be exactly the same, and hence the relative energies of the ring and metal orbitals will be somewhat different, and (*2*) the C_6H_6 system has an additional π-MO which, however, is vacant and of even higher energy than the e_2 orbitals. Thus whatever view one chooses to take of the bonding in the π-cyclopentadienyl metal compounds can also be extended in its general features to a corresponding arene metal system, although the relative importance of the several interactions (in the MO approach) may well change appreciably.

IX. Sandwich-type Metal Compounds of Other Organic Systems

Several metal derivatives have been prepared recently from unsaturated hydrocarbons other than the cyclopentadienyl group and arenes, and these are at least of comparable structural and chemical interest. The bonding of the hydrocarbon system to the metal in these cases must certainly be assumed to be similar to that in the compounds discussed previously, in that it results from overlap of *d* orbitals of the transition metal with delocalized π-orbitals of a carbocyclic system. In this sense the compounds may be distinguished from the well-known metal compounds of olefinic compounds, such as ethylene, of unconjugated diolefins such as dicyclopentadiene and cycloocta-1,5-diene which can function as "olefinic chelate groups," and of acetylenic compounds, although the difference is to some extent merely one of convenience for the purposes of this review.

A. BUTADIENEIRON AND CYCLOHEXA-1,3-DIENEIRON TRICARBONYLS

The compound $C_4H_6Fe(CO)_3$ was first made by Rheilen and his co-workers by the action of butadiene on iron pentacarbonyl (A.12). This preparation was repeated recently (H.11) and a structure (Fig. 20) suggested which is more reasonable than the alkyl type of structure originally proposed. While the new formulation is in keeping with some chemical properties of the compound, e.g., its failure to hydrogenate catalytically (cf. ferrocene) and seems very reasonable, there is so far no direct physical evidence for this structure. Some preliminary high resolution n.m.r. measurements (I.3) suggest that the protons of the terminal methylene groups are not equivalent.

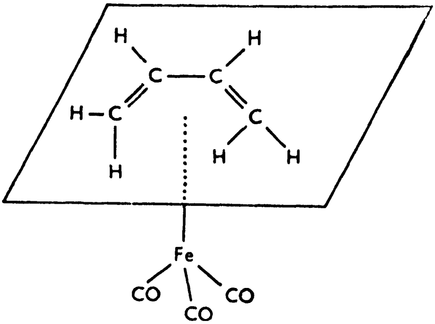

Fig. 20. Structure suggested for ($H_2C{=}CH{-}CH{=}CH_2$)$Fe(CO)_3$ by Hallam and Pauson (H.11; reproduced by permission).

A similar compound, cyclohexa-1,3-dieneiron tricarbonyl was similarly obtained by reaction of the hydrocarbon with iron pentacarbonyl at elevated temperatures in an autoclave (H.11); it was not obtained in a pure state, however.

B. CYCLOHEPTATRIENE AND AZULENE METAL COMPLEXES

As noted before, the tropylium ion, $C_7H_7^+$, has the same number of π-electrons as $C_5H_5^-$ and C_6H_6, and a suggestion was made (F.27) that sandwich-bonded metal derivatives with a C_7H_7 group might be prepared. Although subsequent attempts to obtain such complexes by the reaction of tropylium bromide with sodium salts of anions such as $Mn(CO)_5^-$ and $HFe(CO)_4^-$ did not give the desired product, the direct reaction of cycloheptatriene (tropylidene) and substituted tropylidenes with $Cr(CO)_6$ and $Mo(CO)_6$ has led (H.18,I.6) to the isolation of compounds such as $C_7H_8Mo(CO)_3$ (Table XIV). The structures proposed for these compounds (Fig. 21) again are held to involve sandwich-type bonding. In tropylidene itself, vibrational and n.m.r. studies have indicated that the six olefinic carbon atoms lie in essentially the same plane, and that the π-electron density to some extent by-passes the out-of-plane methylene group, thus giving a quasiaromatic system.

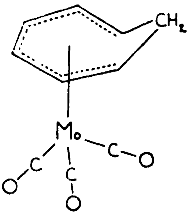

Fig. 21. Structure suggested for $C_7H_8Mo(CO)_3$ by Abel, Bennett, and Wilkinson (H.18; reproduced by permission).

These tricarbonyls, though formally analogous to the arene tricarbonyls, differ in that they are all red in color, while the arene and π-cyclopentadienyl carbonyls of similar formulas are yellow; further, they all show three strong bands in the C–O stretching region, whereas the arene derivatives show only two bands. It is to be expected in the tropylidene carbonyls that owing to incomplete delocalization of the π-electrons, free rotation about the metal–ring axis is impossible and a fixed configuration of the carbon monoxide groups relative to the ring exists; three C–O stretching modes are therefore predicted.

The reaction of cycloheptatriene with iron pentacarbonyl has produced (I.7) a liquid dicarbonyl, $C_7H_8Fe(CO)_2$.

The reaction of tropylium bromide with chloroplatinic acid gives

TABLE XIV. Other Conjugated Olefinic or Aromatic Metal Compounds

Compound	m.p.	Color	Prep.	IR	UV
Group VI					
Cycloheptatriene $Cr(CO)_3$	128–30d.	crimson cryst.	I.6	I.6	
Ditropyl $Cr(CO)_3$		crimson cryst.	I.6[a]	I.6	
Phenyltropilidine $Cr(CO)_3$	d > 150	red cryst.	I.6[a]	I.6	
Methyltropilidine $Cr(CO)_3$	72–73	red cryst.	I.6	I.6	
Cycloheptatriene $Mo(CO)_3$	100 ± 1	orange-red cryst.	H.18,I.6	H.18,I.6	
Ditropyl $Mo(CO)_3$	d > 150	red cryst.	I.6	I.6	
Phenyltropilidine Mo $(CO)_3$	d > 150	red cryst.	I.6	I.6	
Methyltropilidine Mo $(CO)_3$	d > 150	red cryst.	I.6	I.6	
Ditropyl $[Mo(CO)_3]_2$	d > 150	red cryst.	I.6	I.6	
Ditropyl ether $[Mo(CO)_3]_2$	d > 150	red cryst.	I.6	I.6	
Azulene $[Mo(CO)_3]_2$	d > 150	dark red cryst.	H.26	I.7	
Guaiazulene $[Mo(CO)_3]_2$	d > 150	dark red cryst.	I.7	I.7	
Group VII					
[Azulene $Mn(CO)_3]_2$	142–4	yellow plates	I.7	I.7	
Group VIII					
Butadiene $Fe(CO)_3$	19	yellow liq. and cryst.	A.12,H.11,	H.11	H.11
Cyclohexa-1,3-diene $Fe(CO)_3$	8–9	yellow liq. and cryst.	H.11[b]	H.11	H.11
Duraquinone $Fe(CO)_3$			H.8	H.8	
Cycloheptatriene $Fe(CO)_2$	(b.p. 70/0.3 mm.)	yellow liq.	I.7	I.7	
$[C_7H_8PtBr_2]_2$	154.5–55	orange	H.29	H.29	
$C_7H_7PtBr_3$		orange	H.29	H.29	
Azulene $Fe_2(CO)_5$	d > 100	dark red cryst.	I.7	I.7	
$(Azulene)_2Fe_5(CO)_{10}$	d > 180	light brown	I.7	I.7	

[a] Characterized only by infrared spectra.

[b] Not obtained in pure state.

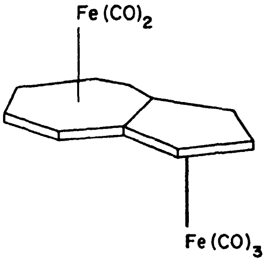

Fig. 22. Proposed structure of azulene$Fe_2(CO)_5$ (I.7).

an orange crystalline precipitate of the tropylium salt (I.6), but the reaction of cycloheptatriene with platinic bromide in acetic acid has been claimed (H.29) to give the compounds $[C_7H_8PtBr_2]_2$ and C_7H_7-$PtBr_3$. The reaction of cycloheptatriene with rhodium trichloride in ethanol (I.7) also leads to a yellow cationic species which may be a tropyliumrhodium compound. The cation $[C_7H_7Mo(CO)_3]^+$, as the fluoroborate, has been obtained from the reaction $C_7H_8Mo(CO)_3$ with triphenylmethyl fluoborate; n.m.r. evidence indicates equivalence of the seven ring protons (I.20).

From the reaction of the blue hydrocarbon, *azulene*, with molybdenum (H.26), manganese, and iron (I.7) carbonyls, complex metal derivatives have also been obtained. Azulene, with fused planar seven- and five-membered rings has only ten π-electrons. Using the inert gas formalism, the compound azulene$Fe_2(CO)_5$ can be formulated as Figure 22. Infrared spectra are consistent with this structure. From molybdenum carbonyl, however, a compound of stoichiometry azulene$Mo_2(CO)_6$ was obtained; unlike the above iron compound, this is paramagnetic and furthermore the Weiss constant is unusually high, perhaps indicating antiferromagnetic behavior. If a molybdenum tricarbonyl group is bound to both the seven- and five-membered rings, two unpaired electrons would be expected; the magnetic behavior, however, suggests considerable spin-spin interaction. The guaiazulene compound is diamagnetic.

C. QUINONE AND TETRACYCLONE METAL COMPLEXES

The irradiation of dimethylacetylene, 1-pentyne, and 3-hexyne in iron pentacarbonyl has led (H.8) to the isolation of compounds such as $Fe(CO)_5(CH_3C{\equiv}CCH_3)_2$. From the infrared spectrum of the dimethylacetylene derivative which showed bands for quinone-like carbonyl groups, Sternberg *et al.* concluded that the product must be considered to have a duroquinone ring directly bound to the metal atom (Fig. 23).

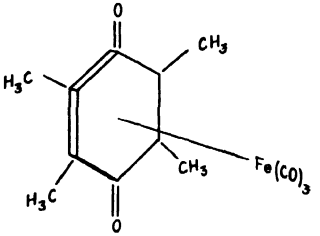

Fig. 23. Structure of the $CH_3C{\equiv}CCH_3$ adduct with $Fe(CO)_5$ proposed by Sternberg, Markby, and Wender (H.8).

Similarly, it has been shown that a compound of the stoichiometry $Fe(CO)_4(\phi{-}C{\equiv}CH)_2$ obtained by treatment of $Fe(CO)_5$ with phenylacetylene in the presence of $Ni(CO)_4$ probably contains a diphenylcyclopentadienone ring bonded through the π-electrons to an $Fe(CO)_3$ group (I.16–I.18).

D. OTHER POSSIBLE SYSTEMS

On theoretical grounds (F.19) it has been considered that by analogy with $C_5H_5^-$ and C_6H_6 it should be possible to bind a cyclobutadiene system C_4H_4 to a metal atom (cf. $C_7H_7^+$ above). An iron carbonyl compound of the correct stoichiometry has indeed been made by Reppe (J.11), but there is as yet no evidence to show that a cyclobutadiene residue is involved in bonding.* Preliminary X-ray data (J. D. Dunitz, private communication) suggest that the compound $(CH_3)_4C_4NiCl_2$, prepared by Criegee and Schröder (I.34), has indeed a four-membered ring, which is, however, probably not square. It is bound to the nickel atom and nickel atoms are joined by chloride bridges in a dimeric molecule.

Several proposals concerning the structures of acetylene metal complexes have been made (see H.28 for references), but the only X-ray determination made to date, by Hock and Mills (H.28), has shown that none of these proposals were correct. The structure found for the but-2-yne complex, $Fe_2C_{12}H_8O_8$, is shown in Figure 24. The two iron atoms are bonded in dissimilar ways. A four-membered

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* The compound of stoichiometry $C_7H_4O_3Fe$ has been shown to be cyclopentadienoneiron dicarbonyl (Green, Pratt, and Wilkinson, unpublished work).

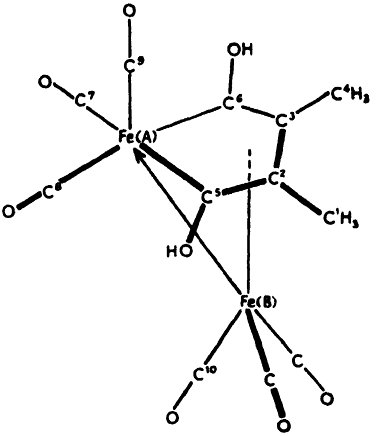

Fig 24. Structure of the but-2-yne complex of iron carbonyl, $Fe_2C_{12}H_8O_8$, found by Hock and Mills (H.28; reproduced by permission).

carbon ring system is bound to Fe(A) by σ bonds. This ring is itself attached to Fe(B) in a manner rather similar to that in the butadiene iron complex discussed previously.

While the atomic arrangement in this structure may well be correct, the postulation that two carbon atoms are σ-bonded to Fe(A) and that two electrons from Fe(B) are donated to Fe(A) is unusual, to say the least, and the electronic structure and bonding may turn out to be different in due course.

This field of acetylene metal derivatives is closely associated with the quinone derivatives noted in the last section, and although these compounds cannot be treated further in the present review, it is fairly clear that many of these complex compounds will eventually be formulated as having delocalized ring systems or delocalized open systems bound to metal atoms in ways in principle very similar to the bonding in the established sandwich compounds.

The question has often been raised as to whether heterocyclic systems can be bound to the transition metals by sandwich bonds. In some cases there seems to be no good reason why this should not happen, although with certain heterocyclics it may be argued that the presence of a hetero atom distorts the electron density so that symmetrical overlap with the metal *d* orbitals is not possible, or that the lone pair electrons on nitrogen, say, prevent such bonding. There have been notes to the effect that thiophen reacts like arenes in substituting in carbonyls, and compounds thiophen$Cr(CO)_3$ (I.22) and thiophen$Fe(CO)_2$ (I.7) have been obtained. The blocking of the donor function in six-membered nitrogen heterocyclics, as in *N*-methylpyridinium iodide, has allowed sandwich compounds to be made from them (I.41).

Certain inorganic cyclic systems, notably the phosphonitrilic halides and their derivatives and the borazines, might also have been expected to behave like arenes, but attempts to prepare metal compounds from them have so far failed.

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* denotes publications of a preliminary character, subsequently expanded by the same authors.

^{R} denotes a Review.

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Interstitial Compounds of Graphite*

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I. Introduction

Graphite is generally considered to be chemically quite inert; it is, nevertheless, able to interact under suitable conditions with a large number of substances. An overwhelming majority of these reactions result in so-called interstitial compounds, which retain certain characteristics of the original graphite structure, suitably modified to accommodate the reactant. The criterion used here to classify a compound as interstitial is the retention of the layer structure of the graphite crystal. The stacking order, bond distances, and even the bond direction may be altered and distorted in some of the interstitial compounds, but the characteristic strong bonding of each carbon atom to three nearest neighbor carbon atoms must be retained. Because of this retention of the graphite layer structure all interstitial compounds can be reconverted to a graphite which bears some resemblance in crystal size or shape to the original starting material.

Three classes of interstitial compounds will be described. In the first class the graphite structure has been altered as extensively as is still compatible with the definition of interstitial compounds; as a result, the properties of compounds in this class differ drastically from the properties of graphite. These compounds are classified as nonconducting compounds, because they lack completely the metallic properties of graphite. The carbon layers of the nonconducting compounds are probably not planar as in graphite, but are buckled or puckered in conformity with the aliphatic nature of these compounds.

The second class of interstitial compounds contains the lamellar compounds. These compounds retain the aromatic, planar graphite layer structure, but contain interstitial monolayers of the reactant in a characteristic distribution between the carbon layers.

The third class of interstitial compounds is comprised of the residue compounds. These are hardly justifiable as true compounds, because they retain the reactant only at imperfections and peripheral surfaces of the graphite crystallites. The properties of residue compounds and of graphite itself differ, however, quite appreciably. It should be pointed out that earlier work on the first two of the three classes of interstitial compounds has been reviewed by several authors, who have treated some of the structural problems in more detail than we have done here (52,57,92,97).

A. STRUCTURE OF GRAPHITE

It is necessary to preface a discussion of the compounds of graphite by a very brief review of the structure of graphite itself. For more detailed reviews of the properties and structure of graphite, several papers (1,26,61) are recommended.

Graphite crystallizes in a layer structure. In each layer carbon atoms are tightly bound to three other atoms. These bonds are considerably shorter (1.415 A.) than carbon single bonds. The

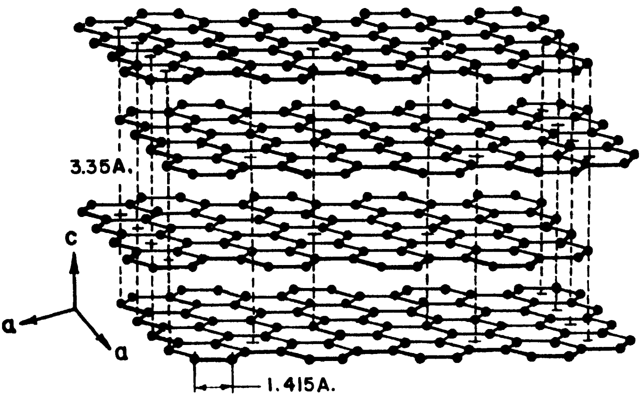

Fig. 1. The hexagonal graphite lattice.

layers are bound together by weak bonds, resulting in a relatively wide separation (3.35 A.) between layers. Alternate layers are displaced relative to each other and are therefore not superimposable by projection perpendicular to the layer planes. Two modifications of graphite exist, the hexagonal form, in which every second layer plane is superimposable (Fig. 1), and the rhombohedral form, in which every third plane is superimposable. The two types of stacking are frequently designated as (ABAB. . .) and (ABCABC. . .) stacking. Recent work by Boehm and Hofmann (8) and by Laves (70) has demonstrated that the rhombohedral modification is frequently present in natural graphite. Even in single crystals, only a minor fraction of the carbon is present in this modification, and it can be removed by heat treatment and reintroduced by mechanical deformation. It is not known whether the two modifications possess different physical properties, although some theoretical work along these lines has been undertaken (40). Differences in the chemical reactivities of the two modifications have been suggested (51) but not confirmed.

II. The Nonconducting Compounds of Graphite

Nonconducting compounds of graphite were discovered long before other interstitial compounds. However, at the present time, only two such compounds, graphite oxide and graphite monofluoride, are known, while scores of other interstitial, particularly lamellar, compounds, have been characterized.

A. GRAPHITE OXIDE

The nomenclature of this compound is still unsettled, graphite oxide is also known as carbon oxide, graphite oxyhydroxide, graphitic acid, or sometimes by the misnomer pyrographitic acid.

Graphite oxide was first prepared by Brodie (9) in 1859. Numerous methods of preparation have since been proposed which involve strong oxidizing agents like concentrated nitric and sulfuric acid mixtures or fuming nitric acid and potassium perchlorate or potassium permanganate (53,120). A modified, rapid method has recently been reported (64).

The endpoint of the oxidation, which usually requires days or weeks, is indicated by fading of the color. The purification of the product is difficult because the acid and oxidizing agent are retained tenaciously. Usually, acetic acid followed by water is used. This treatment may cause some esterification; Ruess therefore recommended omission of the acetic acid wash (112).

1. Composition

Graphite oxide is not obtained as a definite reproducible substance of fixed composition. The reported carbon/oxygen ratios are never lower than two. Graphite oxide invariably also contains hydrogen, part of which is believed bonded as hydroxyl and carboxyl groups (53,123), while part of the hydrogen may be tenaciously retained water (27).

The hydroxyl and carboxyl groups of graphite oxide can be distinguished by their reactivity (16,55). The carboxyl group can be esterified by methyl alcohol and hydrochloric acid, and at least part of the hydroxyl groups can be methylated by diazomethane in dioxane. This methylation is incomplete; only about two-thirds of the hydroxyl groups are affected (16). The total concentration of hydroxyl groups can be determined by estimating the amount of tightly bound hydrogen present after prolonged washing in dioxane. This concentration of hydrogen, corrected for carboxyl groups, is the concentration of hydroxyl groups. Relatively good agreement with this determination is obtained by estimating the concentration of acidic hydrogen in an ion exchange reaction with sodium ethylate.

Most preparations contain approximately one hydroxyl group for six carbon atoms (16,111). Thiele's suggestion that the limiting, ideal composition of graphite oxide is a polymer of $C(OH)_2$ (124) is invalidated by the observation (111) that the concentration of hydroxyl groups never approaches the oxygen concentration in the compound.

It is very likely that most of the oxygen in graphite oxide is bonded by ether linkages to two separate carbon atoms. These linkages were originally thought (53) to be on adjacent carbon atoms, i.e., in ortho positions, but detailed chemical and structural analyses by Ruess (111) have demonstrated that the ether linkages are most probably in meta positions on the same layer plane. Alternate suggestions that the oxygen is present as peroxide groups which "button" adjacent carbon layers (3) or as ionic hydroxide (30) do not appear compatible with the chemical properties of graphite oxide. The meta ether groups might conceivably be hydrolyzed to form the hydroxyl groups known to be present; this hypothesis, however, cannot explain why only a small fraction of the ether links is ever hydrolyzed, nor does it account for the obstinate retention of some hydrogen during drying. More probably, the hydroxyl groups are the result of random disorder among the meta ether links, which will occasionally result in available bonds in para or even more remote positions rather than the required meta position. Oxygen on such a position would presumably not form an ether bridge but, rather, a hydroxyl group. This structural model of graphite oxide was proposed by Ruess (111) and is represented schematically in

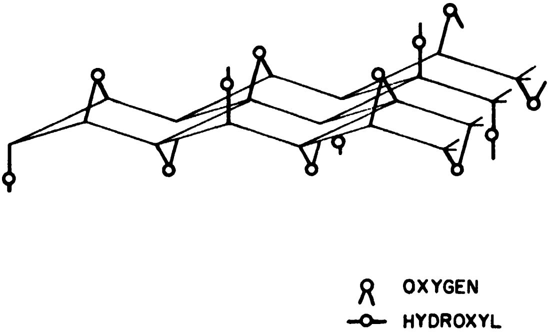

Fig. 2. The structure of graphite oxide, according to Ruess (111).

Figure 2. It should be noted that this model identifies the hydroxyl groups with tertiary alcohol groups.

Hofmann and co-workers have criticized this model by pointing out that the hydroxyl groups of graphite oxide are considerably more acidic than other tertiary alcohols (16). They postulate instead a structure in which hydroxyl groups are vicinal to carbon double bonds; for such a model, the keto and enol tautomeric structures of Figure 3 can be written. This structure predicts an "ideal" composition $C_8O_2(OH)_2$ for graphite oxide.

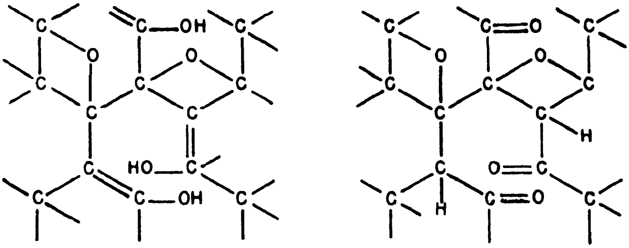

Fig. 3. The structure of graphite oxide, according to Hofmann *et al.* (16).

2. Properties

The color of graphite oxide depends on the C/O ratio, on the water content, and on the presence of solvents other than water. Dry samples are green or brown; they become nearly colorless when hydrated, if the carbon/oxygen ratio is close to two. In nitric acid, the substance is green. The color is not always related to the composition. Light-colored preparations can be converted to darker ones by exposure to light or by dilute alkali without appreciable change in analysis; the lighter and darker forms might well be the keto and enol forms of Figure 3 (16).

The compounds show a series of infrared absorption bands which have been assigned by Hadzi and Novak (37,38) to carbonyl, hydroxyl, and possibly epoxy groups. Identification of these bands was confirmed by methylation or esterification. A band at 6.2 μ was found to become more intense the higher the water content. No bands were found which could be assigned to carbon–carbon double bonds.

The electrical resistance of graphite oxide measured in pellets compressed under 130 atm. was $10^7 \Omega$ cm. at a carbon/oxygen ratio of three, and 4000 Ω cm. at a C/O ratio of 3.5, compared to a value of 0.023 for unreacted graphite (55).

Graphite oxide manifests many of the characteristic properties of colloidal substances (122,128). It swells in water until the individual layers are apparently completely independent. The solution can be filtered, and shows double refraction under flow. The solution is coagulated to a gel by electrolytes. Viscosity measurements at various concentrations were carried out by Thiele and co-workers (121,126). The colloidal particles are negatively charged, probably because hydrogen ions dissociate from some of the hydroxyl and carboxyl groups (122,129). Membranes prepared by evaporating such solutions are semipermeable and have practical uses described in Section V. Biological properties of graphite oxide were described by Thiele and Anderson (127). In the electron microscope graphite oxide is seen to consist of crumpled and folded sheets of apparently high flexibility (5,7,74,85).

3. Structure

The structure of graphite oxide cannot be determined unequivocally by X-ray diffraction, because only a few diffraction lines are observed. An 00*l* line is always present, which indicates that the separation of the carbon layers is approximately 6.2 A. in thoroughly dried samples. When dried samples are allowed to react with water, this layer spacing increases in a continuous fashion. Values as high as 11 A. have been reported. Alkaline solutions produce even larger layer spacings.

The most important problem regarding the structure of graphite oxide concerns the planarity of the carbon layers. It seems very unlikely, particularly in view of the absence of metallic properties, that the carbon layers are planar as in graphite. Since most carbon atoms are attached to four distinct ligands, they are probably tetrahedral; this configuration would cause the layers to buckle. Unfortunately, X-ray studies cannot decide whether such buckling of the planes occurs because no (h,k,l) lines with $l \neq 0$ are observed. Only lines which show the asymmetric line shape (56,111) characteristic of (h,k) lines are found; these are assigned as (20), (02), (22), and (42). The positions of these lines correspond to a distance of 1.44 A. This distance is compatible with a buckled structure in which the X-rays would measure the projections of the single bonds of length 1.52 A. upon a common plane. However, if the layers were not buckled, one would anticipate a distance of about 1.42 A., which is not sufficiently different from the observed value to exclude this structure.

The nonplanar, buckled structure of the layer planes seems to be suggested also by the infrared measurements of Hadzi and Novak (37,38), who note the absence of absorptions attributable to carbon–carbon double bonds and find that the absorption peaks attributed to hydroxyl and carboxyl groups from chemical evidence occur at wavelengths where aliphatic hydroxyl and carboxyl groups normally show absorptions.

The heat of combustion of graphite oxide per unit weight of carbon differs from that of graphite by less than 1% (53). This result is difficult to interpret with any model of the graphite oxide structure, but would seem to favor the model of planar rather than buckled layer planes.

4. Decomposition

Compounds intermediate in composition between graphite and the oxide can be prepared either by incomplete oxidation of graphite or by partial thermal decomposition of the oxide. The results of the two procedures are quite different. Incomplete oxidation results in a mixture of unreacted graphite and graphite oxide, showing diffraction lines of both in variable proportions. Thermal decomposition if carried out slowly (53) causes simultaneous loss of oxygen from each layer plane resulting in a gradual decrease of the layer spacing.

Thermal decomposition of graphite oxide may, however, also occur with nearly explosive violence. If the temperature is not increased very slowly, rapid decomposition usually occurs between 150 and 200°C., releasing H_2O, CO, and CO_2 and producing exceedingly finely divided carbon. This residue contains some oxide and is sometimes referred to as pyrographitic acid. The decomposition also liberates large amounts of heat, which is probably responsible for the difference in the modes of decomposition. During heating the oxygen atoms between the layer planes probably tend to migrate to peripheral surfaces where they react to form mostly CO_2. If the reaction is too rapid, the carbon skeleton is fractured, perhaps first by isolated carbon atoms being torn out of the lattice and later by the mechanical action of the liberated gases; rapid decomposition produces larger amounts of CO than slow decomposition (CO/CO_2 = 1.5 for rapid decomposition; 0.25 for slow decomposition) (52).

The property changes of graphite oxide during slow thermal decomposition were measured by Hofmann and co-workers (52). The ability to swell in water is not lost until the C/O ratio exceeds 4.25, yet the conductivity at this composition is already quite appreciable.

Thermal decomposition of the oxide suspended in concentrated sulfuric acid appears to proceed more gently than dry decomposition. The carbon residue of even the slow thermal decomposition was shown by X-ray diffraction to be graphite of small and imperfect crystallites.

The behavior of the (h,k) diffraction lines during decomposition of the oxide was studied by Matuyama (76). The apparent carbon–carbon spacing determined from these lines decreased during heat treatment, and at 250°C. became less than the value of 1.42 A. for graphite. Heat treatment above 1000°C. was required to restore this spacing to the value characteristic of graphite. These results are particularly difficult to interpret because at 250°C. the layer spacing reverts to the value of 3.35 A. characteristic of graphite, so that the abnormally short bond can probably not be attributed to buckling of the carbon layers.

5. Derivatives of Graphite Oxide

As has been described earlier, various agents cause the layer spacing of graphite oxide to increase. Some of these agents are probably only adsorbed, others are definitely bonded to the compound. Swelling is caused by water, by acetone, which increases the layer spacing to 11 A., by dioxane (I_c = 15 A.), ether (I_c = 8.4 A.), acetic acid (I_c = 12.6 A.). nitric acid (I_c = 12.6 A.), and various alcohols (I_c = 9.6–19.0 A.). Xylene, benzene, and other hydrocarbons cause less or no swelling. The increase in layer spacing caused by various alcohols and by amines was studied by Ruiz and MacEwan, who postulated that ethyl and propyl alcohols arrange themselves parallel to the carbon layer planes (114,115). Higher alcohols are supposed to assume an orientation perpendicular to the layer planes because of space limitations. The possibility of attributing some of these spacings to multiple layers of the swelling agent was apparently not considered. Evidence for such multiple layers was advanced by Ruess for graphite oxide exposed to dioxane. Spacings as high as 24 A. have been reported for graphite oxide containing both water and aromatic amines.

It is not likely that swelling in alcohols actually produces organic derivatives of graphite oxide rather than merely addition complexes. Amines probably form salts with the acidic groups. The number of actual organic derivatives of graphite oxide is surprisingly small. The methylation products, with layer spacings of 8.5–9 A. in the dry state, obviously belong to this category. Chlorination of the carboxyl groups is possible and produces essentially an organic derivative (16), but an extensive organic chemistry based upon graphite oxide is apparently not possible.

The principal obstacle to performing organic reactions with graphite oxide is the relative ease with which the oxide can be reduced to graphite (54,92,111) by reducing agents like potassium iodide (but not bromide), by NH_3, or by a number of aromatic amines, like aniline, methylaniline, dimethylaniline, and trimethylaniline (but not aliphatic amines). Most of the reducing agents remove only about half the oxygen of the oxide; incomplete reduction is also caused by ferrous chloride or hydrazine in acid solution, but hydrazine in alkaline solution causes much more extensive reduction, together with occlusion of large amounts of water which is very difficult to remove from the product (56).

Reaction of graphite oxide with hydrogen sulfide apparently results in a transitory graphite sulfide analogous to the oxide; this compound decomposes gradually, but occludes a large amount of sulfur in the final product. Hofmann and Frenzel (54) determined a layer spacing of less than 4 A. for this product. Hadzi and Novak noted the absence of infrared absorption bands in this substance and concluded that no sulfide compound was present (37,38).

B. GRAPHITE MONOFLUORIDE

1. *Preparation*

Graphite fluoride is the only other known nonconducting compound of graphite. It is obtained by the direct interaction, which is occasionally explosive, of fluorine and graphite (113). Under unfavorable conditions this reaction produces volatile carbon fluorides such as CF_4, but at 450°C. the only product of the reaction is solid CF. The synthesis of the compound was shown by W. and G. Rudorff

(103) to be unexpectedly involved, successive preparations under apparently identical conditions often produced entirely different products. These products differed in composition, color, layer spacing as determined by X-rays, and apparent density. Black products of composition $CF_{0.676}$ and layer spacing I_c of 8.9 A. were sometimes obtained; occasionally the white product $CF_{0.988}$ with I_c = 6.6 resulted; more often gray products were formed. These products were not intermediates from a complete fluorination. If a reaction was terminated before completion, X-ray analysis showed the presence of both unreacted graphite and a final product of only one layer spacing, which might have any value between 6.6 and 8.9 A. (103). Apparently, some unknown conditions during the peripheral attack of the graphite layer planes determined the composition and I_c spacing of the initial product, which was faithfully copied by the remainder of the graphite during fluorination. Attempts to fluorinate a dilute compound with a large layer spacing to a more concentrated compound were not successful.

2. *Properties*

Apparent densities of the graphite fluorides were determined by W. and G. Rudorff in a xylene or heptane pycnometer. The results were completely unexpected. The densities of the compounds apparently increased with decreasing fluorine content, thus with increasing *c* spacing, and were considerably higher than calculated. The explanation was found to be the ability of xylene and heptane to penetrate the compound without appreciably changing the *c* spacing; apparently the incompletely fluoridated products contained more void space to admit these organic solvents.

The electrical resistance of graphite fluoride was determined by Ruff and Bretschneider (113) on powder compacts at 140 atm. to be in excess of 3000 Ω cm. as compared to 0.03 Ω cm. for unreacted graphite.

Graphite fluoride shows none of the swelling and colloidal properties which are characteristic of graphite oxide. Although acetic acid or hydrocarbon solvents were found to wet the fluoride, no swelling or solution occurred.

3. *Decomposition*

Thermal decomposition of graphite fluoride occurs similarly to the oxide either in a gentle fashion, if the temperature is raised slowly, or explosively, when heating is too rapid.

During gentle decompositions, the reversion to graphite is a discontinuous process; the layer spacing of the fluoride does not change, but the characteristic lines of graphite appear and gradually increase in intensity.

Reduction of graphite fluoride can also be accomplished by zinc and acetic acid (113), resulting in a product of specific resistance 1.25 Ω cm., i.e., about 40 times higher than the original graphite.

4. *Structure*

Like the oxide, graphite fluoride yields only 00*l* and a few (*h,k*) lines in powder diffraction studies. Early studies by F. Ebert (113) were apparently carried out on an incompletely reacted compound of $I_c = 8.2$ A. The interesting suggestion was made that the compound is completely ionic, C^+F^-, with planar carbon layers; if correct, this structure would render the compound exceedingly interesting for a study of the band structure of the lower conduction band of graphite. W. and G. Rudorff have shown, however, that the compound is very probably covalent, the layer spacing is not very different from the sum of two covalent carbon fluorine bond lengths (C–F = 1.4 A.) plus two Van der Waals' radii of fluorine (2.55 A.).

As in graphite oxide, buckling of the planes is suggested but not confirmed by the projected carbon–carbon distance of 1.46 A. calculated from (*h,k*) lines (103). The buckled structure is further suggested by an infrared absorption of the fluoride at a frequency similar to where fully fluorinated aliphatic compounds absorb (99).

C. DILUTE STAGES OF NONCONDUCTING COMPOUNDS

It should be pointed out in anticipation of subsequent sections that the mechanism of formation and decomposition of nonconducting compounds differ not only among these compounds, but differ even more when compared with lamellar compounds. In the formation of the fluoride and the oxide both graphite and the final product are present until conversion is complete. The decomposition of the fluoride is again a similar process. However, the oxide decomposes in a gradual manner; only one solid phase at a time is present which loses oxygen continuously. In lamellar compounds of graphite, formation and decomposition occur in a completely different fashion in which many highly ordered intermediate stages of the compounds are present. The formation of these intermediates will later on be attributed to the ionic character of the lamellar compounds. In analogy, the absence of such intermediates seems to suggest that the nonconducting compounds are not ionic or even partly ionic, and lends further support to the model of tetrahedral carbon atoms and puckered or buckled layer planes in these compounds.

III. Lamellar Compounds

A. CLASSIFICATION

Lamellar compounds of graphite always manifest certain common structural and electrical properties. X-ray diffraction studies show the reactant in these compounds to be present in planar layers, generally only one molecule thick, which are separated by a number of carbon layers of graphitic structure, i.e., with layer spacings of 3.35 A. (along the *c* axis of Fig. 1) and *a* spacings of 1.415 A. and a hexagonal stacking of alternate layers (ABAB... structure, Fig. 1). In lamellar compounds, the number of these carbon layers between layers of reactant depends upon the conditions of preparation. The number can be decreased by increasing the concentration or activity of reactant. This number of carbon layers, i.e., the ratio, *n*, of carbon layers to reactant layers, is usually defined as the *stage* of the particular lamellar compound. For a given external concentration or vapor pressure of reactant, the stage seems to be fixed throughout the compound when equilibrium has been reached. The electrical conductivity of lamellar compounds usually exceeds considerably the conductivity of graphite.

Lamellar compounds of graphite are formed when any one of the reactant substances listed in Table I reacts with graphite. The structure of many of these lamellar compounds has been determined by X-rays and electrical measurements have been made on a number of them. They always manifest those common properties which have been generalized as defining lamellar compounds of graphite. It must be understood that these properties have not yet been deter-

TABLE I
Substances Which Form Spontaneous Lamellar Compounds with Graphite

Reactant	Mole ratio, C/R	Ref.	Reactant	Mole ratio, C/R	Ref.
Sb_2O_4	1850	21	$PtCl_4$	48	21
$HfCl_4$	1310	21	$CuS_{1.3}$	46	21
$K_2Cr_2O_7$	1000	21	$SbCl_5$	46	21
$Ba(MO_4)_2$	850	21	$TaCl_5$	38	21
$EuCl_3$	710	21	$SmCl_3$	35	21
$RuCl_3$	560	21	$AuCl_3$	33	21
$V_2S_{3.5}$	460	21	$ZrCl_4$	25	21
$CuBr_2$(?)	446	21	UCl_4	25	21
$Cr_2S_{3.5}$	438	21	YCl_3	22	21
$Sb_2S_{4.8}$	317	21	$BiCl_4$(?)	18	21
$CuCl_2$(?)	270	21	$PdCl_2$(?)	18	21
$YbCl_3$	235	21	$InCl_3$	18	21
NO_2(?)	(?)	91	CrO_2Cl_2	16	25
$PdS_{2.2}$	153	21	Cl_2	16	44
$WS_{2.4}$	132	21	Br_2	16	94
$RbCl_3$	119	21	CrO_2T_2	15	21
$GdCl_3$	115	21	$CuCl_x$(?)	13	21
$IrCl_4$	111	21	$TlCl_3$	11	21
MoO_3	99	21	$CoCl_x$(?)	11	21
WCl_6	94	21	$FeCl_3$	8	125
$ReCl_4$	87	21	K	8	116
$DyCl_3$	79	21	Rb	8	116
BCl_3(?)	79	21	Cs	8	116
FeS_2	72	21	CrO_3	6.8	21
$MoCl_5$	68	21	ICl	5	44
TlS_2	59	21	$CrCl_3$(?)	4	21

mined for some of the compounds derived from the reagents listed in Table I, but it is confidently assumed that these will manifest the same features once they are prepared in sufficient purity and examined by suitable means. For lamellar compounds whose structure has not yet been determined by X-rays, the concentration is usually described by the ratio C/X, of carbon atoms to molecules of reactant. This index is given in Table I for the most concentrated lamellar compounds prepared from the reagents listed. The compounds have been arranged in order of decreasing values of C/X. As a consequence the table lists lamellar compounds roughly in order of increasing stability. Additional chemical reagents listed in Table II are classified as electrolytic rather than spontaneous to distinguish the method by which they can be reacted with graphite.

TABLE II
Substances Which Form Electrolytic Lamellar Compounds

Reactant	Ratio, molecule/ ions	Mole ratio, C/R	Ref.
CH_3NH_2	5	~150	29
NH_3	5	~150	29
$BF_3(CH_3COOH)_2$			107
CF_3COOH	1.5	30	107
H_2F_2	2	8	96
H_3AsO_4			95
H_3PO_4			95
H_2SO_4	2	8	95
H_2SeO_4		8	95
$HClO_4$		8	95
HNO_3		8	95

B. SPONTANEOUS LAMELLAR COMPOUNDS

As the name implies, these compounds are for medby the spontaneous interaction of graphite and the reactant. They are usually prepared by reacting graphite with liquid or vapor of the reactant in closed systems for several hours, at temperatures where the vapor pressure of the reactant is at least several millimeters of mercury. Uniform reaction of all the graphite present is usually insured by reacting in a closed system. Most frequently, a two bulb system is employed, the graphite being placed in one glass or quartz bulb connected by a constriction to a similar bulb containing the reactant. Both bulbs are evacuated to facilitate mixing and generally the graphite is maintained at a somewhat higher temperature than the reactant to prevent excess reactant from accumulating. The reaction is terminated either by sealing off the constriction connecting the two reaction bulbs or, when convenient, by quenching to temperatures where the vapor pressure of the reactant is negligible.

Substances which form spontaneous lamellar compounds are of widely varying types (Table I). Some are elements, but the vast majority are metal halides, metal oxides, and metal sulfides. Many of the entries in Table I are due to recent systematic studies of molecular lamellar compounds by Croft (21–25). Unfortunately, Croft made no effort to exclude excess halogen from his reaction mixtures. As a consequence he reported many compounds which are actually ternary lamellar compounds (Section III-D). In some instances where considerable excess of halogen was known to be present these compounds are designated with a question mark in Table I.

A compound with nitrogen dioxide, also designated with a question mark in Table I, was reported by Reyerson and Wertz (91) to be formed from graphitized carbon black. In our laboratory we were unable to form such a compound from natural or artificial graphites.

1. *Composition*

The analytical procedures used to characterize lamellar compounds in Table I differ necessarily, but they are nearly always rendered somewhat inaccurate by the fact that spontaneous lamellar compounds are only stable as long as excess reagent is present to maintain equilibrium. If this excess reagent is removed for purposes of analysis, the compounds inevitably decompose somewhat. The amount of decomposition can often be minimized by quenching the compound while excess reagent is still present. Subsequent washing in suitable solvents is followed by standard analytical procedures. For some compounds this procedure is not practicable because the reactant can still be leached out of the compound even at relatively low temperatures. Croft reported that most lamellar compounds formed from the halides of Group IIIA metals are decomposed rapidly by washing with water at room temperature. Actually Rudorff's (102) and also our (50) experience indicates that such hydrolysis probably occurs with all lamellar compounds although at different rates.

The complications of solvolysis can occasionally be avoided by analyzing the compound in the presence of excess reagent. Lamellar graphite bromide has been analyzed by Hooley (59) by weighing the compound within the reaction vessel with a quartz fiber balance. Even this procedure may be rendered inaccurate by adsorption or capillary condensation.

Most spontaneous lamellar reactions are carried out with the vapor of the reactant, but some reactions of this type have been studied in solutions. For example, potassium reacts with graphite at room temperature from a NaK solution (50), bromine from solutions in CCl_4 (47), etc. On the other hand, solutions of $FeCl_3$ in molten salts will actually decompose a graphite ferric chloride compound, presumably because the activity of $FeCl_3$ is low in such solvents. Most of it is present as $FeCl_4^-$ (36).

Until recently, the reasons why certain substances form lamellar compounds with graphite were not well understood. As a consequence, a large number of substances which fail to react have been tested for such compound formation. In Table III are listed some of these substances. A surprising fact, apparent from Tables I and III, is that many substances of similar chemical properties may differ in their reactions toward graphite.

TABLE III
Substances Which Do Not Form Lamellar Compounds with Graphite (21,108)

CuCl	$TiCl_4$	$BiCl_3$	$LaCl_3$	CdI_2	ThI_4	$MnCl_2$	BrCN
$BeCl_2$	$SnCl_2$	VCl_4	$CeCl_3$	Hg_2Cl_2	PCl_3	$CoCl_2$	NOCl
$MgCl_2$	$SnCl_4$	SO_2Cl_2	$PrCl_3$	CCl_4	PCl_5	$NiCl_2$	NOBr
$CaCl_2$	$PbCl_2$	$SOCl_2$	$NdCl_3$	$SiCl_4$	$AsCl_3$	$PdCl_2$	NO
$BaCl_2$	$PdCl_4$	$SeOCl_2$	$ErCl_3$	$GeCl_4$	$SbCl_3$	$PtCl_2$	N_2O
$ZnCl_2$	$ThCl_4$	$TeCl_4$	$ScCl_3$				

C. ELECTROLYTIC LAMELLAR COMPOUNDS

In contrast to the spontaneous lamellar reactants, the number of electrolytic reactants is quite small. The substances tabulated as electrolytic in Table II do not react spontaneously with graphite. They can, however, be induced to react by auxiliary oxidizing or reducing agents which do not themselves enter into combination in the resulting lamellar compound. This auxiliary agent is most conveniently an external electric battery. For example, graphite bisulfate is formed from the anode when concentrated sulfuric acid is electrolyzed between graphite and an auxiliary cathode (58, 100). The anode reaction can be written as

$$C_m + 3\ H_2SO_4 \rightarrow C_mHSO_4 \cdot 2\ H_2SO_4 + H^+ + e^- \qquad (1)$$

where the quantity m is variable and depends only on the quantity of electricity passed. After prolonged electrolysis a stage 1 compound is formed with a value of $m = 24$. The method of preparation indicates rather convincingly that the electrolytically prepared lamellar compounds are salt-like and ionic; this group of compounds has in fact often been designated as graphite salts.

The concentrated stage of the bisulfate compound can also be obtained by reacting graphite and sulfuric acid with auxiliary oxidizing agents like Mn^{3+}, Mn^{4+}, MnO_2, $KMnO_4$, HNO_3, CrO_3 and others (58,100).

1. *Composition*

Chemical analyses of the electrolytic compounds is sometimes simplified by the fact that they do not have to be stabilized by thermal quenching as the spontaneous compounds do. In principle the electrolytic compounds are unstable as soon as the auxiliary oxidizing or reducing agent is removed or the electrolytic current is turned off. Nevertheless, the compounds cannot decompose unless an impurity is present which can exchange electrons with the compound. Unreacted graphite (100) or, in some cases, water can act in this way, but, in the absence of suitable oxidizing or reducing agents, such compounds remain unchanged for long times. Thus, the bisulfate compounds can be washed free of excess sulfuric acid by phosphoric acid, various aliphatic hydrocarbon solvents, carbon tetrachloride, chloroform, or carbon bisulfide. Organic solvents containing oxygen are, however, oxidized, and even benzene and toluene are apparently converted to the corresponding sulfonic acids. This metastability of electrolytically prepared compounds even at the temperature of formation renders them particularly useful for many property studies as will be described in Section III-K-2.

The analytical procedure for determining the composition of the compounds containing acid was essentially two-fold (58,100). The content of acidic anion was evaluated from the consumption of oxidizing agent during formation or by decomposition of the compound with a measured quantity of reducing agent. The content of excess acid was estimated by suitable washing and subsequent analysis. It was confirmed by pycnometric measurements of the volume of acid displaced during the reaction in conjunction with microscopic or X-ray diffraction studies on the volume increase of the graphite during reaction. The ratios of excess acid molecules to acidic anions have been listed in the second column in Table II.

The only electrolytic compounds prepared thus far in which the graphite is reduced instead of oxidized are the amine compounds

(29). These substances were prepared in liquid amine or ammonia. Compounds more concentrated than about $C_{200} \cdot NH_4 \cdot 4NH_3$ decomposed spontaneously.

It is curious that only a small number of electrolytic compounds have been prepared. Because of their enforced stability this class of compounds appears to hold promise for practical applications particularly if they could be prepared from reagents stable at high temperatures. At one time it was believed that only oxygen acids were capable of forming electrolytic compounds. Later, however, the hydrofluoric acid (96) and the amine compounds (29) were shown to exist. It might be inferred from Table II that hydrogen must be present in the compound for stabilization. On the other hand, it might be speculated that any ionic liquid, M^+X^- which is either difficult to oxidize or to reduce, should, in analogy with equation 1, form electrolytic compounds at graphite anodes or cathodes according to

$$C_n + 3\,M^+X^- \rightarrow C_n{}^+X^- \cdot 2MX + M^+ + e^-$$

$$C_n + 3\,M^+X^- + e^- \rightarrow C_n{}^-M^+ \cdot 2\,MX + X^- \qquad (2)$$

A number of molten salts listed in Table IV were in fact tested by us in this way, but no evidence for compound formation has been detected either at the graphite anodes or cathodes. This work has, however, not yet been abandoned.

TABLE IV

Substances Which Do Not Form Electrolytic Lamellar Compounds

Reactant	Temperature
KCl	800
NaCl	825
LiCl	625
KF	900
KI	740
$PbCl_2$	520
LiCl-KCl	450
Li_2SO_4	875
$C_2H_4(NH_2)_2$	25
$C_6H_5NH_2$	25
$(C_6H_5)_2NH$	25
C_5H_5N	25
$C_3H_7NH_2$	25

D. TERNARY LAMELLAR COMPOUNDS

The lamellar compounds derived from the substances listed in Tables I and II differ not only in the method of preparation but also in complexity. Most of the substances listed in Table I (with the possible exception of substances designated by a question mark) form binary systems with graphite. The substances in Table V all form ternary lamellar compounds which contain two different chemical species besides graphite. A number of ternary spontaneous lamellar compounds have also been prepared, mostly in our laboratory (28) in attempts to understand the bonding in lamellar compounds (see Section III-L). Many of the species which form ternary lamellar compounds with graphite, will not react by themselves but require the third component for stabilization. Generally the mole ratio of the two reacting species remains fixed at all concentrations of the compound. Electrical measurements will be described which indicate that in these compounds the species present at the smaller concentration is ionized. It is anticipated that a systematic study will reveal a vastly larger number of ternary lamellar compounds than is known at present.

E. INCOMPLETE LAMELLAR COMPOUNDS

The author feels that certain contradictions in the literature on lamellar compounds can be resolved by classifying some lamellar compounds in the separate group of incomplete lamellar compounds. These are by definition compounds which are not in equilibrium with excess reagent and will actually undergo structural changes during attempts to equilibrate them. Apparently no lamellar compound can be washed without some decomposition occurring. Rudorff (102) and also the author (50) have observed that any solvent capable of removing excess reactant will also cause some decomposition of any lamellar compound. The rate of this decomposition varies widely. Apparently the reactant is most rapidly leached from the peripheral areas of the crystals, which may occasionally "button up" and release further reactant very slowly. Structure determinations of incomplete lamellar compounds resulting from excessive washing show the presence of finite amounts of unreacted graphite mixed with the lamellar compound. Incomplete compounds frequently manifest density inhomogeneities on a microscopic scale. A very careful structure determination by Cowley and Ibers (20) was carried out on such an incomplete lamellar compound of graphite with ferric chloride. If an incomplete lamellar compound of this type is heated after washing (20), it may become homogeneous, presumably because the reactant layers expand and reinvade the depleted regions. It has never been shown whether this expanded incomplete compound is complete again, i.e., is in equilibrium with some characteristic vapor pressure of reactant, or will rearrange to a lamellar compound of a higher stage. Another type of incomplete lamellar compound may be obtained by the equally dangerous procedure of subliming off excess reagent *in vacuo*. This procedure has occasionally been utilized to prepare more dilute stages of a compound from a concentrated stage. As long as the resulting compound is not shown to be truly in equilibrium with a definite vapor pressure of reactant, it may well be an incomplete lamellar compound. A third type of incomplete compound is sometimes obtained when a concentrated compound is decomposed and subsequently equilibrated for a short time only with reactant at a lower vapor pressure or concentration. The removal of excess reagent is occasionally very sluggish. For certain

TABLE V
Ternary Lamellar Compounds of Graphite

Reactant		Ratio A/B in compound	Ref.
A	B		
$AlCl_3$	Cl_2	6	28
$AlCl_3$	Br_2	6	28
$AlCl_3$	I_2	6	28
$AlCl_3$	$FeCl_3$	3	28
$GaCl_3$	Cl_2	6	102
$HgCl_2$	Cl_2	12	98
$CdCl_2$	Cl_2	25 (?)	98
NH_3	Na	2	106
NH_3	K	2	48, 106
NH_3	Rb	2	106
NH_3	Cs	2	106
NH_3	Ba		50
NH_3	Ca		50
NH_3	$FeCl_3$	6	104
CH_3NH_2	Li	1.7	106
Na	O_2		50
Cs	Na	8	51

types of graphite it is practically always incomplete (see Section IV on residue compounds). As a consequence this procedure may result in lamellar compounds which still contain excess reactant. Incomplete lamellar compounds of this kind may differ considerably from complete lamellar compounds. We demonstrated such differences in the electrical properties (44). Herold (51) reported considerable differences in equilibrium pressures between incomplete and complete lamellar compounds of bromine. He also noted the absence of such differences in the alkali metal compounds of graphite. This result is in agreement with the known behavior of lamellar alkali metal compounds not to form residue compounds.

The formation of incomplete lamellar compounds can apparently be avoided best by reacting graphite with reactant vapors in the two bulb method described above, preparing a given compound only from less concentrated stages, and taking great care in subsequent purifications.

As a matter of speculation it is conceivable that a fourth type of incomplete lamellar compound may be formed by cooling a true compound very far below the temperature at which it was formed. The reactant layer, which was originally contiguous throughout each crystal, may contract during cooling into a more densely packed layer, resulting in parts of the crystal being bared of reactant. Such a transformation suggested by Cowley (20) has never been demonstrated conclusively for true lamellar compounds but ought to be looked for by structure determinations of lamellar compounds at very low temperatures.

F. STRUCTURE

Repeated reference has already been made to X-ray studies of lamellar compounds. Such studies are absolutely essential to the complete characterization of each compound. They determine the composition which corresponds to first stages of the compound, the size of the reactant layer in the compound, and in some instances the location of reactant atoms or molecules relative to the positions of the carbon atoms.

1. Historical

The first X-ray studies of chemically characterized (69) lamellar compounds seem to have been carried out by Hofmann and Frenzel

(58) wno studied graphite bisulfate since 1930. The alkali metal compounds of graphite were investigated in detail by Schleede and Wellmann (116) in 1932. Their conclusions were confirmed and amplified in later investigations by Rudorff (105) and by Herold (51). Ferric chloride compounds of graphite were studied in 1932 by Thiele (125) and again in 1940 by Rudorff and Schulz (104). A very detailed re-examination of these compounds was published in 1956 by Cowley and Ibers (20) who supplemented X-ray diffraction studies by electron diffraction techniques. Graphite bromide was first studied in 1941 by Rudorff (94). The largest number of different stages of one compound have been examined by Rudorff (93,105) who characterized by X-ray diffraction the graphite bisulfate and the potassium graphite compounds of stages 1–5.

2. Stages

The structure determinations have shown that most carefully prepared lamellar compounds can exist in several concentration stages which differ in the number of carbon layers alternating in a definite periodic sequence with single layers of reactant. These sequences are shown in Figure 4 as determined by Rudorff and Schulze (105) for five stages of the potassium compounds of graphite. The most concentrated compounds usually are a first stage, in which single layers of carbon alternate with single layers of reactant; for some reactants, however, the second or even higher stages are the most concentrated forms known. No lamellar compound has ever been found to contain multiple layers of one reactant.

The strict periodicity of carbon and reactant layers shown in the example of Figure 4 may be characteristic of relatively concentrated compounds only. Although some compounds are strictly ordered even at a stage 5, others become disordered at higher concentrations. This disorder was demonstrated by Maire and Mering (75) for graphite bromide, in which only the second stage contained an ordered sequence of carbon and reactant layers. More dilute stages were reported to contain monolayers of bromine in random interlayer positions. The order might possibly have been improved by prolonged annealing, which is known (105) to improve the ordering in lamellar compounds.

For a limited number of reactants the structure of the most con-

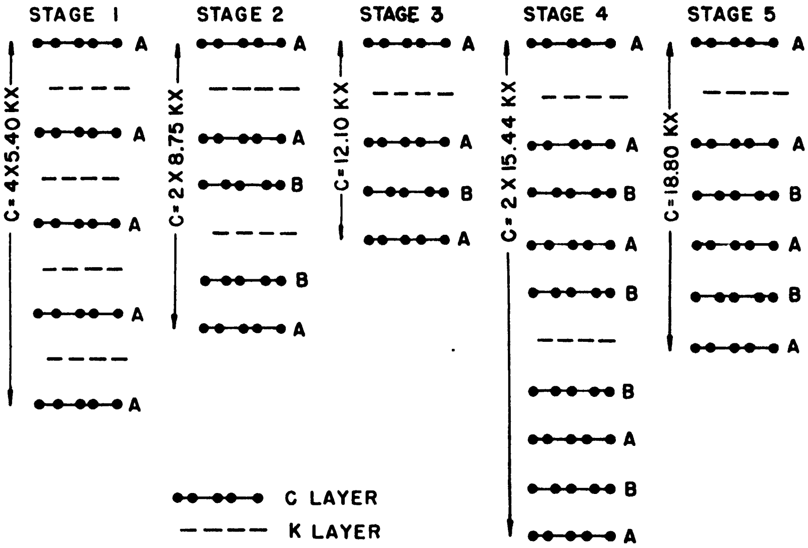

Fig. 4. Section of carbon skeleton in several stages of graphite potassium (105)

centrated and of several dilute stages has been derived from X-ray diffraction studies alone. In Table VI the interlayer spacings of a number of compounds have been listed together with the stages which have been identified. Not all compounds yield equally sharp and complete X-ray spectra. For dilute compounds, the lines sometimes become sharper at compositions corresponding to definite stages of the compound. At other compositions, the lines are more diffuse presumably because the more concentrated and the more dilute compounds are intermingled randomly. However, some compounds show indefinite patterns even at definite compositions, sometimes even at the composition corresponding to a first stage. In these cases the diffuse pattern may be due to surface contamination of excess reactant, particularly if the reactant scatters X-rays strongly, or to inherent high mobility of the atoms or molecules of the reactant within the structure. For those compounds which yield only few diffraction lines, one can still generally identify a series of 00*l* lines. The structure determination is then supplemented by measuring two other physical properties. The expansion of a graphite single crystal during the formation of the compound in combination

TABLE VI
Stages and *c* Spacings of Lamellar Compounds

Reactant	Stage	Minimum I_c[a]	D[b]	Reactant	Stage	Minimum I_c[a]	D[b]
HNO_3	1	7.84	4.49	$InCl_3$	2	12.80	6.10
	2	17.14	4.44		3	16.20	6.15
	3	14.49	4.44	CrO_2Cl_2	2	14.6	7.9
	4	17.84	4.44		or 1	14.6	3.95
	5	21.19	4.44	K	1	5.40	2.05
H_2SO_4	1	7.98	4.63		2	8.75	2.05
	2	11.33	4.63		3	12.10	2.05
	3	14.72	4.63		4	15.46	2.06
	4	18.09	4.63		5	18.80	2.05
	5	21.46	4.63				
$HClO_4$	1	7.94	4.59	Rb	1	5.65	2.30
	2	11.12	4.32		2	9.02	2.32
	3	14.30	4.25		3	12.34	2.29
	4	17.65	4.25		4	15.75	2.35
	5	21.00	4.25		5	19.08	2.33
H_3PO_4	2	11.3	4.6	Cs	1	5.94	2.59
$H_4P_2O_7$	2	11.5	4.8	$Li(NH_3)_2$ $Na(NH_3)_2$ $K(NH_3)_2$	1 2	6.6 9.9	3.25 3.20
Br_2	2	10.4	3.70				
ICl	1	10.58	7.23 (?)				
$FeCl_3$	1	9.37	6.02	CF_3COOH	1	8.2	4.85
	3	16.21	6.16		2	11.52	4.82
$FeCl_3 \cdot 3\ AlCl_3$	1	9.52	6.17		3	14.85	4.90
$Cl_2 \cdot AlCl_3$	1	9.62	6.27	$BF_3(CH_3CO_3H)_2$	1	8.08	4.73
	2	12.80	6.10		2	11.30	4.60
	4	19.65	6.25		3	14.60	4.55

[a] Separation of reactant layers.

[b] D = apparent thickness of reactant layer.

with the measured 00*l* lines often determines the stage of the compound. The microscopic measurements can be confirmed or replaced by density measurements in a pycnometer. Such combined diffraction and density measurements do not always yield unambiguous results, however. As an example, for the most concentrated lamellar compound of iodine chloride (108), the diffraction pattern determined the identity period, I_c, to be some multiple of 7.05 A. The density measurements indicated a three-fold volume increase of the graphite during reaction. This increase is compatible only with an identity period of 3 × 7.05 comprising two carbon planes. The structure is therefore either a first stage compound, with an interlayer spacing of 10.58 A., or a second stage compound with a spacing of 17.8 A. for the layers containing ICl.

3. *The Carbon Skeleton*

The separations and orientations of the carbon atoms within the carbon layer planes have never been found to change as a result of lamellar compound formation.

The orientation relative to each other of the carbon layers within various lamellar compounds can sometimes be deduced from the magnitude of the I_c values. For example (93), the $(11l)$ lines of odd-numbered stages ($n = 1$, $n = 3$, and $n = 5$) of the nitric acid and the perchloric acid compounds yield I_c values which comprise only n carbon layers, while even-numbered stages ($n = 2$, $n = 4$) yield I_c values which comprise $2n$ carbon layers. For compounds of odd-numbered stages, therefore, the two carbon layers adjacent to each reactant layer are not displaced parallel to the layer planes, as adjacent layers would be in the absence of reactant, because such a displacement would result in a doubling of the I_c values. For even-numbered stages, the observed doubling of the I_c values indicates that the carbon layers adjacent to each reactant layer are again not displaced parallel to the layer planes and that adjacent carbon layers not separated by reactant are so displaced. Designating the reactant layer by R, the hexagonal stacking of graphite (ABAB. . .) has become (ARARA. . .) or (ABRBARA. . .).

Similar structural analyses have shown that in the alkali metal compounds (105), and the CF_3COOH compounds (107), the carbon layers adjacent to layers of reactant, are not displaced perpendicular to the c axis. However, such a displacement was observed in the bromide (94), the ferric chloride (104), and the H_2F_2 (95) compounds. The graphite bisulfate compound (93) shows a singular behavior; apparently two different modifications of the stage 1 compound exist, one with displaced, the other with undisplaced, carbon layer planes (ARBRA. . .) and (ARARA. . .).

In dilute compounds, the relative orientation of those carbon layer planes which are in contact with other carbon layers is always the orientation characteristic of graphite itself; i.e., the (ABAB) structure. In this connection it should be mentioned that the rhombohedral modification, which is occasionally present in graphite in as high a proportion as 30%, can be eliminated by formation of a lamellar compound and subsequent recovery of the graphite from the compound. It might be anticipated that this rearrangement can only be promoted by those lamellar compounds, such as the alkali metal or nitric acid compounds, which disarrange the typical graphite layer stacking. However, numerous tests by Boehm and Hofmann (8) have shown that this ability to destroy the rhombohedral modification is also shared by ferric chloride, bromine, and chromyl chloride and therefore does not depend upon the details of layer plane stacking in the lamellar compound.

4. The Reactant Skeleton

The most difficult part of the structure analysis of lamellar compounds concerns the distribution and orientation of the reactant. Such analyses seek solutions to four different problems: the arrangement of the reactant species in a given layer, the relative orientation of neighboring reactant and carbon layers, the orientation of neighboring reactant layers relative to one another, and the orientation of individual molecules of reactant within each layer. Solution to the first three problems has in part consisted of determining the multiplicity of the identity periods (i.e., how many carbon and reactant layers are contained in one repeat distance), which is found from values of the *hkl* lines of powder and of single crystal patterns. Solution of the fourth problem concerning the orientation of individual molecules has been sought by determining the intensity differences of related diffraction lines. Exact solution of these problems by constructing Fourier contours from the diffraction lines has only been attempted once (20).

The monolayers of the reactant do not usually retain the structure of pure solid reactant, nor do they assume a random arrangement as in a liquid state. Instead, the atoms or molecules of the reactant are arranged on a lattice which tends to be closely related to the vicinal graphite lattice. Some compounds assume triangular or hexagonal arrays. Two possible arrangements of these arrays are shown in Figure 5, together with one adjacent carbon layer plane. The arrangement of Figure 5*b* seems to account best for the diffraction patterns of concentrated alkali metal and bisulfate compounds. It is obvious that Figure 5*b* can apply only to those compounds in

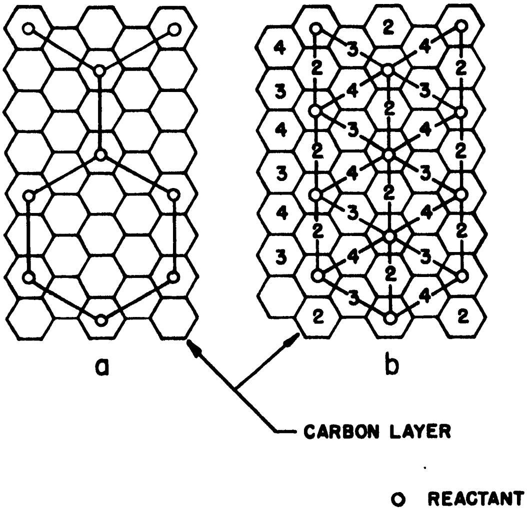

Fig. 5. Distribution of reactant in some $C_{12}R$ and C_8R lamellar compounds.

which the ratio of carbon atoms to reactant species is 8 or a multiple of 8, whereas for Figure 5*a* this ratio is a multiple of 12.

Substances which, in dilute lamellar compounds, occupy the more loosely packed array of Figure 5*a* are occasionally found to change to the tighter packing of Figure 5*b* in concentrated compounds with a corresponding change in stoichiometry. Rudorff and Schulze (105) have demonstrated this transition in the alkali metal compounds between stages 2 and 1.

A similar transition involving a tightening of the reactant structure was observed by Maire and Mering (75) at the second stage of the graphite bromide compound. They did not report any detailed structural analysis of this tightening. Similarly, the ferric chloride compound can, according to Rudorff, exist in either a loose or a tight structure in the first stage, depending on the external vapor pressure of ferric chloride. This conclusion has been disputed by Cowley and Ibers (20), who claim that a ratio for carbon to $FeCl_3$ of 5.8 is retained in several compounds of various concentrations which they examined; any excess of carbon above this ratio was present as unreacted graphite. These and other inconsistencies in the structural analysis of the ferric chloride compounds suggest that incomplete rather than true lamellar compounds were used for either or both of these determinations.

It is of considerable interest whether the reactant lattice repeats throughout the crystal without lateral displacement along the *a* axes (Fig. 1). This arrangement of different reactant layers relative to one another is not known for any dilute lamellar compounds, and is known for the first stage of only a few compounds. In the first stage of the alkali metal compounds, neighboring reactant layers are indeed displaced laterally. In fact, all possible lateral displacements consistent with Figure 5*b* seem to occur. Rudorff and Schulze (105) postulated that neighboring layers are displaced alternately along the two *a* axes by 2.45 A., so that the potassium atoms occupy progressively the positions indicated by numbers in Figure 5*b*. Thus only every fifth alkali metal layer is superimposable by displacement along the *c* axis without additional displacement parallel to the layer plane. This displacement of successive layers was postulated to explain the experimental observation that the I_c value for the alkali metal lattice is four times the interlayer spacing.

In the first stage of the graphite bisulfate compound the reactant layers show a different type of lateral displacement. In this compound, the I_c value is three times the interlayer spacing. According to Rudorff (93) this observation is consistent with a model in which neighboring layers are displaced by 1.63 A. along both *a* axes, so that only every fourth reactant layer is superimposable without lateral displacement. Rudorff also reported the curious observation that the structure applied to only one of two possible modifications of the first stage of the bisulfate compound. In the other modification, which differs also in the arrangement of neighboring carbon atoms to each other as described earlier, the acid layers are apparently randomly distributed.

In the ferric chloride compound, Fourier analysis (20) of electron diffraction rings indicates a preference for a superimposable orientation of reactant layers in adjacent layer spaces. Only about half of the chlorine atoms succeed in attaining this preferred superimposable structure.

The complete characterization of the reactant skeleton requires determining the spatial orientation of individual reactant molecules in the layer planes. For atomic reactants this problem obviously does not exist. Rudorff (93) has pointed out that the orientations

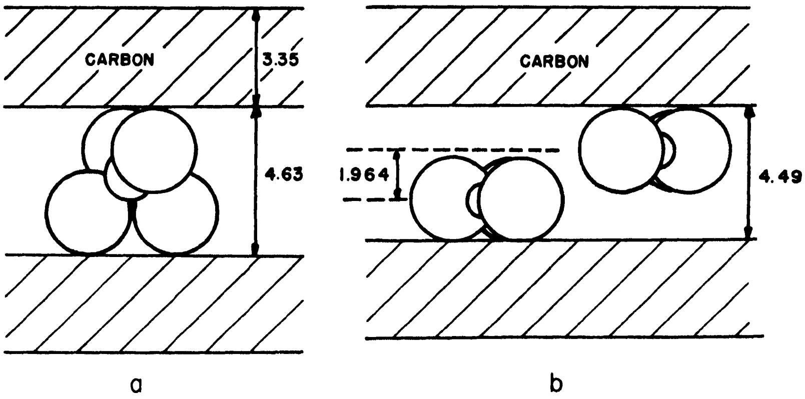

Fig. 6. Orientations of acid molecules in graphite compounds (93).

of nitric, sulfuric, selenic, and probably also perchloric acids in their concentrated lamellar compounds can be estimated from the intensity ratios of the 00*l* lines. He compared the observed intensities with values calculated for a number of probable orientations and concluded that the sulfuric, selenic, and perchloric acid molecules prefer the arrangement shown in Figure 6*a*. The nitric acid molecules apparently prefer the alternating distribution of Figure 6*b*.

Ferric chloride in its lamellar compounds is oriented in such a way that the iron atoms are situated on planes halfway between the carbon layer planes, and the Cl atoms on two planes parallel to and 3.36 A. distant from the carbon layer planes. The ferric chloride molecules are distorted (20) from their structure in the pure solid apparently as a result of attempting to assume preferred positions relative to the adjacent carbon layers.

It might be thought that the orientation of the reactant molecules in the layer planes could be calculated from their space requirement which determines the repeat distances, I_c. As used here, I_c is the separation of reactant layers. Unfortunately this method is not reliable. One difficulty concerns the choice of the space requirement along the *c* axis for the carbon layer. It appears reasonable to allow the same value of 3.35 A. as in graphite for the carbon layer in the compounds. The value $I_c - 3.35\,n$ for a stage *n* compound should then be a measure of the diameter of the reactant molecule. For the alkali metal compounds, this method leads to improbably small diameters for the metal atom, i.e., 2.05 A. for K, and 2.30 A. for Rb. These are considerably smaller than the atomic diameters and smaller even than the ionic diameters of the metals. Anticipating the results of the electrical measurements, these discrepancies are believed to confirm that the alkali metal reactants are at least in part positive ions, and that in consequence they penetrate into the *p* electron cloud which determines the thickness of 3.35 A. of the carbon layers. For most of the other reactants the choice of 3.35 A. for the carbon layer is probably more realistic, because the reactant, if ionized, is negatively charged and will not penetrate the *p* electron cloud.

The apparent thickness of the reactant layer (D) for several substances is listed in Table VI. The value is usually constant at different concentration stages of the same compound. In a few compounds, significant contractions occur between different stages.

Table VII lists the apparent densities and the space requirements ($I_c - 3.35\ n$) for a number of lamellar compounds. These are compared with the densities of the pure reactants and the ionic

TABLE VII
Space Requirement of Reactant in Lamellar Compound

	Density		Diameter	
Reactant	In lamellar compound	Pure	In lamellar compound	Ionic
HNO_3	1.1	1.55 (*l*)	4.49	4.62[a]
H_2SO_4	1.7	1.84 (*l*)	4.63	4.69[a]
$HClO_4$	1.7	1.76 (*l*)	4.59	
H_2F_2	1.49	0.99 (*l*)	4.70	
CF_3COOH	1	1.5 (*l*)	4.85	4.5
Br_2	3.42	3.12	3.70	3.92
ICl	2.67[b]	3.18	7.23 or 14.45	6.3[c]
$FeCl_3$	2.13	2.8	6.02	[d]
$InCl_3$	2.8	3.5	6.10	[d]
$6\ AlCl_3 \cdot Cl_2$	1.66	2.44[e]	6.17	6.72[f]
$K(C_8K)$	1.51	0.86	2.05	2.66
$K(C_{24}K)$	1.005	0.86	2.05	2.66
$Rb(C_8Rb)$	2.94	1.53	2.30	2.92
$Rb(C_{24}Rb)$	1.96	1.53	2.30	2.92
Cs	4.06	1.87	2.59	3.38
$M(NH_3)_2$			3.25	3.05[c]

[a] Figure 6.
[b] Pycnometer determination.
[c] Main axis of reactant parallel to *c* axis.
[d] Reactant has nearly same *c* spacing in lamellar compound as in pure solid.
[e] For major constituent.
[f] Tetrahedral arrangement of Figure 6A.

diameters of the reactants estimated for a probable geometric configuration in the lamellar compound.

Agreement between the densities calculated for the reactants within the lamellar compounds and the densities of pure reactants is generally poor. Part of this lack of agreement may be due to the tendency of the reactant to occupy a lattice closely related to the graphite lattice. This effect cannot influence the space requirement calculated from measured layer spacings. This space requirement is actually found to agree rather well with ionic diameters of the reactants. It should be noted that ionic instead of molecular diameters are listed in the table because the reactant is known from electrical measurements to be partly ionized in the lamellar compounds. It can be concluded that in most compounds the carbon layers are separated only far enough to admit the ions and molecules of the reactant. Notable exceptions appear to be the nitric and hydrofluoric acid compounds. For unknown reasons, the layer separation in these is considerably wider than required. Even an arrangement in which the fluoric acid molecules are aligned perpendicular to the layer planes requires less (about 3.6 A.) than the observed spacing of 4.7 A.

Other inferences from Table VII are that bromine molecules are oriented parallel to the layer planes and the ICl molecules are oriented perpendicular to the layer planes. Even in this arrangement the calculated spacing of 6.27 A. does not agree with the observed values of 7.23 or 14.45 A.

G. KINETICS

Invasion of graphite by lamellar reactants can occur either by concerted attack at all layer planes or by stepwise invasion of a limited number of layer planes leading to progressively more and more concentrated stages. Apparently the second mode of attack occurs during the electrolytic or chemical formation of graphite bisulfate. The second and first stages of this compound show a very distinct blue color, which appears only late in the reaction and, furthermore, spreads from some peripheral point rapidly across the whole surface even of large flakes of graphite (50). If the invasion were a concerted attack at all layers planes, the color should be observed at the edges of the crystals from the beginning of the reaction and should spread gradually across the crystal. Unfortunately, such a simple color test has not been performed with spontaneous lamellar reactants. There exists, however, evidence that at least some spontaneous lamellar compounds are formed by simultaneous attack of the reactant at all layer planes. Barker and Croft (4) reported that the reaction of ferric chloride with graphite was a diffusion-controlled invasion of the planes under conditions where a stage 1 compound ultimately resulted. The results were, however, far from simple. They were explained partly by two diffusion constants, one about ten times larger than the other. The fast rate, which was found to require an activation energy of 3.1 kcal per mole of $FeCl_3$, dominated until the concentration of $FeCl_3$ reached 75% of saturation. Wherever this concentration was exceeded, the slow diffusion rate took over, with an activation energy of 2.7 kcal per mole. This interpretation is particularly attractive because Rudorff and Schulz (104) have suggested from structural analyses and reactivities that part of the ferric chloride is bound less tightly in the compound than the remainder. This suggestion has, however, been disputed by Cowley and Ibers (20), as discussed in detail in Section III-F. The interpretation of the diffusion experiments implies that the diffusion rate in crystals of different diameter should depend upon the square of the diameter. A much smaller dependence upon size was actually observed. In our opinion part of this difficulty must be attributed to an unfortunate choice of analytical procedures. The ferric chloride content was always estimated by washing the crystals in water. This procedure probably removed part of the reactant, and undoubtedly a larger part in the smaller crystallites. It is not clear whether this analytical procedure had an appreciable effect on the main conclusions of Barker and Croft's work.

Measurements of the reaction rate of bromination have been carried out by Wertz (91). These studies showed that the reaction is initially fast but continues at an extremely slow rate. No satisfactory kinetics has been found to describe the interaction. In contrast, the reactions of alkali metals with graphite were reported by Herold (51) to be relatively fast and essentially complete in a matter of a few hours.

H. HEATS OF REACTION

The heat evolved during lamellar reactions has been measured calorimetrically for the few compounds listed in Table VIII. For the three alkali metals K, Rb, and Cs the heat of transformation from a second stage to a first stage compound has been estimated by Herold (51). The transformation causes a distinct change in color from blue to golden. Herold determined the equilibrium vapor pressures at which this color change occurred and calculated the heat of reaction from the temperature dependence of the equilibrium pressure. He obtained a value of 3.5 kcal. per gram atom of potassium for this transformation. For rubidium and cesium, the heats of this reaction were determined as 5.85 and 10.1 kcal., respectively.

TABLE VIII
Heats of Reactions, $-\Delta H$, of Lamellar Compound Formation

Reactant	$-\Delta H$, kcal./g. atom C.	Ref.
K	1500	32
K	970	90
$FeCl_3$	2700	104
H_2SO_4 (+ HNO_3)	400	100

I. STABILITY

The relative stability of lamellar compounds can approximately be estimated as in Table I from the concentration in the most concentrated compound. A better index of stability is the stage, determined by X-rays, of the most concentrated compound. A quantitative measure of stability is the partial molar free energy and its dependence on concentration. For volatile reactants this quantity can be calculated from measured vapor pressures of the reactant in equilibrium with the lamellar compound. Relatively few such measurements have thus far been carried out. Furthermore, some of these require the rather involved recalculations carried out below. The free energies will be utilized later in theoretical discussions of the bonding in lamellar compounds.

1. Vapor Pressures

The customary procedure of synthesizing spontaneous compounds in two connected bulbs maintained at slightly different temperatures lends itself admirably to measurements of equilibrium vapor pressures. Such measurements have been reported for the alkali metal compounds (51) and the halogen compounds of graphite (47,51,75).

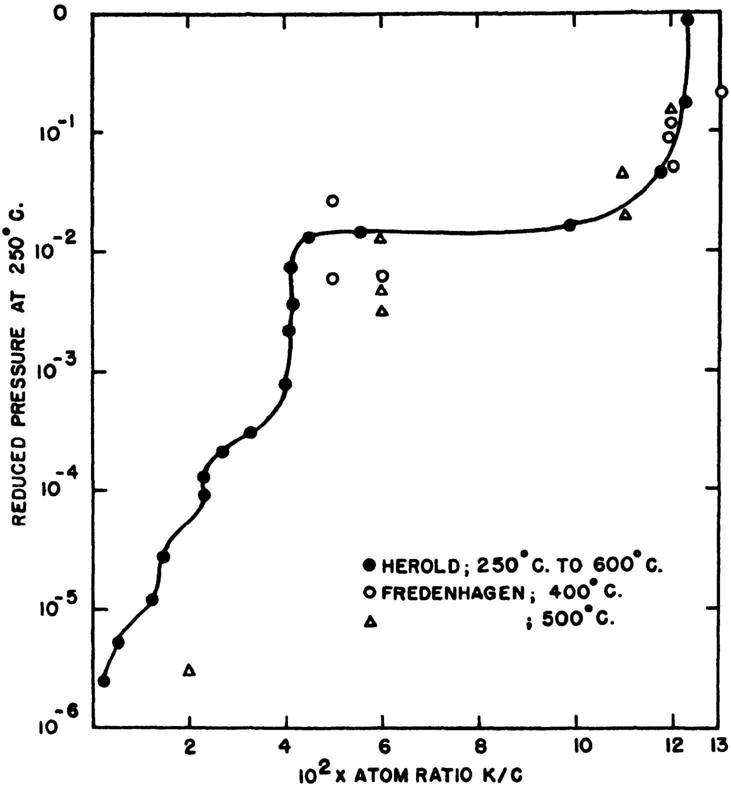

Fig. 7. Equilibrium vapor pressures of potassium graphite.

Two modifications of the method have been used. Every investigator except Herold maintained the graphite samples at the same temperature, but varied the temperature of the bulb containing the reactant to control the composition of the product. Herold reversed the procedure and varied the temperature of the graphite to control the composition of the product; this method allows more precise control of conditions yielding dilute compounds. Although Herold undoubtedly obtained the most precise results, these cannot be represented by isothermal plots of equilibrium pressure vs. composition. For each composition the pressure is measured at a different temperature. For this reason, Herold did not even report his results in terms of pressures. We have calculated from Herold's

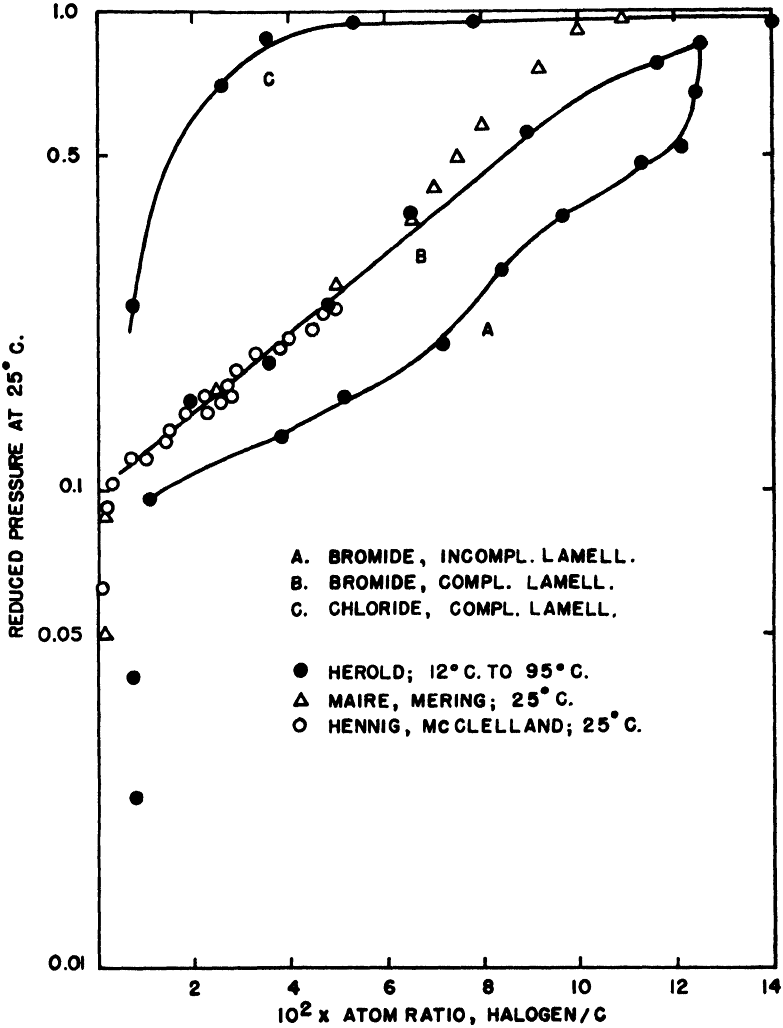

Fig. 8. Equilibrium vapor pressures of graphite halides.

results what may be called "reduced" equilibrium pressures. For thermodynamic reasons to be discussed below the reduced equilibrium pressure is defined as $(p/p_0)^{T/T_0}$, the ratio of the equilibrium pressure p to the saturation pressure p_0 of pure reactant at the temperature of the compound in question raised to a power T/T_0, the ratio of the measuring temperature to a standard T_0. These data have been plotted in Figures 7 and 8 together with the isothermal plots of other investigations. The equilibrium pressure curves show a series of inflections which occur at compositions corresponding to definite stages of the compounds.

Figure 8 also shows the vapor pressures of "incomplete" lamellar graphite bromide (see Section III-E) obtained by debrominating a fully brominated compound. At any given vapor pressure, this incomplete compound contains more bromine than the lamellar compound, because of a retained residue.

Isothermal vapor pressures of graphite bromide have also been reported by Juza and co-workers (66). These have not been included in Figure 8 because they are not equilibrium data. The compounds were prepared at initially high and gradually decreasing bromine pressures and are therefore intermediate in composition between incomplete and true lamellar compounds.

The agreement between differently determined equilibrium pressures in Figures 7 and 8 is gratifying and appears to support the method of calculating reduced equilibrium pressures.

The procedure of recalculating Herold's data in terms of "reduced pressures" is justifiable only if the entropy of the reaction is small. The argument runs as follows: the formation of a compound, say, the potassium compound, from the elements

$$\mathrm{K}(l,\, T_1) + \mathrm{C}_n(s,\, T_1) \rightarrow \mathrm{C}_n\mathrm{K}(s,\, T_1) \tag{3}$$

is characterized by a free energy change ΔF. The partial molar free energy, $\overline{\Delta F}$, of infinitesimally increasing the concentration of this compound, involves evaporation of liquid potassium ($\Delta F_e = 0$), expanding the vapor from p_0 to p, and reacting at equilibrium ($\Delta F_r = 0$), hence

$$\overline{\Delta F} = RT_1 \ln p/p_0 \tag{4}$$

The corresponding partial molar entropy is

$$-\overline{\Delta S} = \partial\overline{\Delta F}/\partial T = \partial/\partial T(RT \ln p/p_0)$$

neglecting small Δpv terms for the condensed phases. Thus, if the partial molar entropy change is small, $(p/p_0)^T$ will be temperature independent and can be related for a set of data obtained like Herold's data over a range of temperatures. The condition of small entropy change can actually be tested for some of Herold's data. He reported values from which the equilibrium pressures at several temperatures can be calculated. The values apparently pertain to the same concentrations of metal compounds intermediate in composition between the final and second stages; in fact, Herold assumed that the pressures are characteristic of the equilibrium:

$$2\,M(l, T) + C_{24}M \rightleftharpoons 3\,C_8M(s, T) \qquad (5)$$

The calculated entropies per mole of liquid metal, M, are −1.8 e.u. for the graphite potassium compound, +1.8 e.u. for graphite cesium, and +3.3 e.u. for graphite rubidium. The positive values are unexpected. A negative entropy is expected for reaction 5, which results in a considerable volume contraction and ordering. However, the relatively small values of the entropy seem to justify the treatment of Herold's data in terms of "reduced" pressures.

The reasons for the small or positive values of the entropies of reaction 5 may be the relative disorder of the compounds of compositions intermediate between definite stages of compounds. It is very desirable to obtain similar entropy values over a wider range of compositions.

The equilibria of the ferric chloride–graphite system have not yet been studied exhaustively. The measurements reported to date (104) indicate that this system is more complex than most other lamellar compounds. Apparently, the third stage of the compound transforms directly into the first stage at the saturation pressure of $FeCl_3$ at 300°C. Equilibria at stages lower than the third have not been measured. The second stage has been prepared only by an indirect method which may result in an incomplete lamellar compound. At temperatures lower than 300°C., saturated $FeCl_3$ vapor will form the first stage. Above 300°C. only the third stage is stable and above 400° only very much more dilute compounds (a 16th stage is estimated from the reported composition). Apparently at temperatures above 300°C., the compounds are rendered unstable for reasons discussed in the next section. The equilibria should therefore be studied below 300°C., even though the reaction is quite slow at these temperatures.

2. Free Energies

In the author's opinion, the most general lamellar reaction which is likely to involve small entropy changes at all concentrations is a reaction of solid reactant R yielding solid products

$$R(s, T) + C_n(s, T) \rightarrow C_nR(s, T) \tag{6}$$

Since the partial molar free energies of such solid-solid reactions are expected to be temperature insensitive, they should afford a reliable test of relative reactivities for various reactants.

To calculate partial molar free energies for reaction 6 from equilibrium data measured for reactions like 5, one must estimate the free energy of

$$R(s, T) \rightarrow R(l, T) \tag{7}$$

This calculation is somewhat hazardous because most reactions are studied above the melting point of the reactant, so that equation 6 has only hypothetical meaning. The free energy of 7, except for changes in *pv*, is

$$\Delta F = -(L_m/T_m)\,\Delta T + \Delta C_p\,(\Delta T - T\,ln\,T/T_m) \tag{8}$$

where L_m = the heat of melting at the melting temperature T_m; ΔC_p = the difference in heat capacity of solid and liquid R; and $\Delta T = T - T_m$.

From the published data of Herold, partial molar free energies of the solid-solid reaction 6 were calculated and plotted in Figure 9. It is seen that the potassium compound is more stable at nearly all compositions than the halogen compounds; however, in this representation, the chlorine compound is considerably more stable than the bromine compound. Herold concluded from the high equilibrium pressures of the chlorine compound at room temperature that chlorine only adsorbs on graphite but does not form a lamellar compound. We feel that his results are due to the measurements having been carried out considerably above the melting temperature of chlorine (ΔT in equation 8 exceeds 100°). The existence of a truly lamellar chlorine compound is confirmed by electrical (44) and by magnetic (67) measurements, and also by the high chlorine content (C_6Cl) of some compounds measured by Herold, which can hardly be attributed to adsorption. Nevertheless, X-ray diffraction studies at

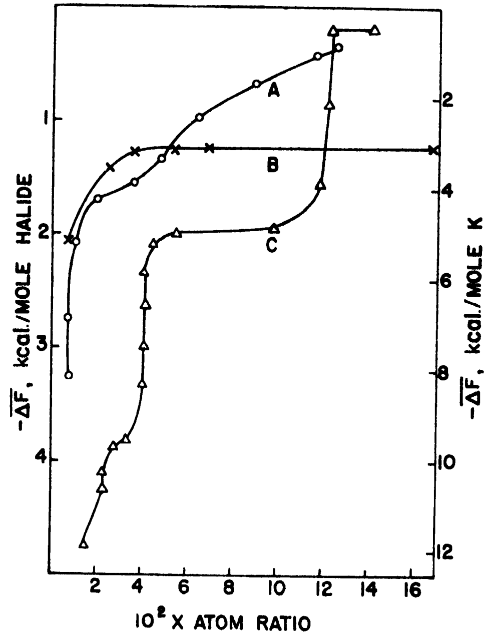

Fig. 9. Partial molar free energies of graphite compounds. *A*, C_nBr (left-hand scale); *B*, C_nCl (left-hand scale); *C*, C_nK (right-hand scale).

low temperature are highly desirable to ascertain whether chlorine forms lamellar compounds.

Equilibria for electrolytic lamellar compounds can be measured with considerable precision. It is merely necessary to determine the electrode potential of the compound against a standard electrode; this potential corrected for the reference potential determines the partial molar free energy. Such measurements have been carried out for the graphite bisulfate compound, using a mercurous sulfate (43) or a hydrogen (100) reference electrode. Inflections were observed as in other lamellar compounds at composition corresponding to the concentrated stages of the lamellar compounds.

J. OPTICAL PROPERTIES

Concentrated lamellar compounds frequently show very characteristic intense colors. Surprisingly enough, no detailed studies of the optical properties of such compounds have been published. The colors are predominantly blue, but the intensity and depth of the color differ for various reactants. Examples of blue compounds are the first stage of the acid compounds, the second stage of the alkali metal compounds, the first stage of Cl_2–$AlCl_3$ compounds, and concentrated UF_6 (50), WS_2, and CrO_3 (21) compounds of unknown stage. The color of concentrated alkali or alkaline earth amine compounds is blue or sometimes purple. The first stage of the alkali metal compounds is golden yellow.

The appearance of the characteristic color usually occurs abruptly. the bisulfate turns blue when the graphite has been oxidized by exactly one equivalent per 48 carbon atoms. Herold's publications seem to indicate that the change from a blue to a golden color occurs for alkali metal compounds of composition intermediate between the first and the second stage.

K. ELECTRICAL PROPERTIES

1. History

The electrical properties of lamellar compounds should in principle be measured on single crystals, but such measurements are very difficult because sufficiently large crystals are rarely obtainable. As a consequence, most such measurements have been obtained on compounds derived from artificial polycrystalline graphite or on powder compacts.

The first measurement of the magnetic properties of lamellar compounds was reported in 1940 by Rudorff (104), who determined the magnetic susceptibility of the ferric chloride compound and concluded that reduction of ferric to ferrous chloride had not occurred in the compound. Ganguli (33) measured the diamagnetic susceptibility of what he assumed to be a bisulfate compound. Actually his method of preparation is now known to yield a residue compound rather than a lamellar compound. Goldsmith (34) measured the susceptibility of graphite bromide in 1950 and concluded that covalent or ionic bonds are formed between carbon and bromine.

Electrical conductivities of graphite compounds were investigated for the first time by Rudorff and Schulz (104), who reported that powder compacts of the ferric chloride compound showed similar or occasionally much higher resistances than graphite powders.

Investigations carried out by Novick (83) in 1944 but published only in 1956 have shown that bromine increases the conductivity of graphite very considerably. McDonnell, Pink, and Ubbelohde (78) investigated powder compacts of concentrated lamellar compounds and showed that graphite bromide conducted ten times better and potassium graphite fifty times better than pure graphite. The susceptibility and thermoelectric power of these compounds were also measured. The experiments were interpreted as evidence that electrons are transferred from graphite to bromine in the bromine and from potassium to graphite in the metal compound.

Quantitative measurements of this electron transfer were obtained by us for a considerable number of lamellar compounds by determining the concentration dependence of conductivities, Hall effects, and other electrical properties (43,45,28,29).

2. Concentrations of Donors and Acceptors

There exists little doubt that transfer of electrons between graphite and reactant occurs during the formation of all the lamellar compounds whose electrical properties have been investigated. Based upon this observation it has been proposed (43,46) that a lamellar compound can be formed only if such an electron transfer occurs. How this transfer may stabilize the resulting compound is discussed in Section III-L-3.

Lamellar compounds will be classified as *n*-type or *p*-type according to the terminology appropriate to semiconductors to designate whether electrons have been transferred to the graphite (*n*-type) or from the graphite (*p*-type). It is convenient to introduce here the concept of donor and acceptor to designate the chemical species which actually donated or accepted the electron from the graphite.

For a limited number of compounds the donor or acceptor concentration can be measured directly. As described in Section III-C, electrolytic lamellar compounds can be formed in such a way that the charge transfer occurs through an external circuit. Since this charge is equal to the donor or acceptor concentration, the electrical properties can be measured directly as a function of the known ion concentration. For nonelectrolytic compounds, the donor or acceptor concentration is assumed to be the same as for electrolytic compounds of identical electrical properties. This assumption implies that electrical properties of all *p*-type or of all *n*-type compounds are equal at equal acceptor or donor concentration.

This procedure has been justified by the following argument. The electrical properties are known to depend upon the electron population of the conduction band and thus upon the acceptor or donor concentration. They may or may not depend also upon the chemical identity, size, polarizability, etc., of the reactants, but if they do, this chemical effect will almost certainly influence the resistance more than the Hall coefficient. Such a specific chemical effect was therefore shown to be absent by demonstrating that cross plots of Hall effects against resistances coincide for several different lamellar compounds (45).

Comparison of the acceptor or donor concentration determined by these electrical measurements with the total reactant concentration, determined analytically, has shown that the reactant species is always partially ionized. Complete ionization as suggested by McDonnell *et al.* (78) apparently never occurs.

In those compounds which have been analyzed by electrical measurements, the ionized fraction of the reactant is approximately constant at all concentrations of the compound and is usually one-third to one-fourth. In the halide compounds the composition was determined as $C_n^+ \cdot X^- \cdot 3X_2$, in the potassium compounds approximately as $C_n^- \cdot K^+ \cdot 4K$. An attempt was made to increase this fractional ionization of the potassium lamellar compounds by adding ammonia, which is absorbed by these compound in considerable amounts at room temperature. A reduction of the electrical resistance due to additional ionization was, however, not observed. This failure of ammonia to increase the donor concentration seems to imply that the fractional ionization of potassium is not altered. The results may, however, also be interpreted as evidence that the fractional ionization of potassium is increased, but is compensated by ejection of an equivalent amount of potassium from the lattice because of the space requirements of ammonia. This experiment should be supplemented by electrical measurements of the fractional ionization in potassium amine compounds prepared in liquid ammonia (106). In ternary compounds one of the components is usually completely ionized (28), viz., $C_n^+ \cdot Cl^- \cdot 3AlCl_3$; $C_n^+ \cdot Br^- \cdot 3AlCl_3$; $C_n^+ \cdot Cl^- \cdot FeCl_2 \cdot 3AlCl_3$, etc.

The interhalogen compounds of graphite are also essentially ternary compounds. Electrical measurements have not been carried out on these. A stoichiometry of $C_n^+ Br^- \cdot (IBr)_4$ appears likely for the iodine bromine compound because chemical analysis of this compound by Colin and Herold (17) yielded a bromine: iodine ratio of 1.22:1. This interpretation of the analysis of the iodine bromide compounds appears more reasonable to us than the suggestion of Colin and Herold that the halogen ratio is unity and the analytical value of 1.22 is due to experimental errors. The fractional ionization of ternary compounds has thus far been determined only in cases where the two reactants are present in a concentration ratio of 3:1 or 4:1. Apparently some ternary compounds exist in which this ratio is considerably larger. According to Rudorff, lamellar compounds are formed by mercuric chloride, indium chloride, and cadmium chloride in which the concentration ratios of metal halide to excess chlorine are 6:1, 30:1, and 21:1, respectively. It is anticipated that the excess of chloride in these compounds provides only part of the total acceptors and that lower valence states of the metal halide constitute the remainder. On the other hand, the lower valence states of indium and particularly of cadmium are ordinarily not particularly stable. In fact, the existence of the univalent state of cadmium has not even been conclusively demonstrated, although it has been postulated to explain the conductivity of molten cadmium chloride containing dissolved cadmium (35). A systematic determination of the acceptor concentration by electrical measurements of lamellar compounds of mercuric chloride, indium chloride, and

TABLE IX

Fractional Ionization in Two Metal Halide Compounds

R (reactant)	Cl/C,[a] $\times 10^3$	R/C, $\times 10^3$	Accept/C, $\times 10^3$	R/accept
$Cl_2 \cdot HgCl_2$	1.13	7.6	2.43	3.1
$Cl_2 . CdCl_2$	[b]	2.18	0.26	8.4
		5.55	0.83	6.7
		8.55	1.29	6.6
		8.73	1.14	7.7
		8.95	1.40	6.4
		9.4	1.26	7.4
		9.85	1.57	6.3
		12.65	1.85	6.8

[a] "Excess" chlorine, which liberates iodine from KI.

[b] Reliable analyses for Cl have not been obtained. Considerably more Cl is consumed during synthesis than is released during analysis.

cadmium chloride is therefore particularly desirable. We carried out a few preliminary determinations after we were informed by Rudorff (98) of the existence of such compounds. These isolated measurements, made on compounds which were not completely homogeneous, are represented in Table IX and suggest that the metal halide is reduced to an appreciable extent in these compounds.

The electrical measurements demonstrate conclusively that most lamellar compounds are only incompletely ionized. The measurements do not reveal whether the charge is shared equally by the molecules involved or is localized on one ion. The author feels that this distribution varies from compound to compound. In graphite bisulfate, the charge is very probably localized on the bisulfate ions; similarly, in some ternary compounds, it will be localized on only one of the chemical species present. In the halides and the ternary compounds the charge is probably localized if the compound contains isolated halide ions, as implied by such stoichiometric formulas as $C_n^+ \cdot Br^- \cdot 3Br_2$, etc. However, these formulas may not represent correctly the actual structure of the reactant. The stoichiometry is equally well represented by $C_n^+ \cdot Br_2^- \cdot 2.5Br_2$ or $C_n^+ \cdot AlCl_4^- \cdot 2AlCl_3$, etc. The presence of such molecular ions was originally suggested (11) for graphite compounds of metal halides by Rudorff and Landel (102) and will be discussed again in Section III-L-8. If molecular ions are present, the charge probably resonates between all the reactant molecules present, thereby stabilizing the compound. In substances like the alkali metal graphite compounds, the positive charge is also probably shared equally between the atoms.

At the present time the most important deduction from the electrical measurements on lamellar compounds has been the classification into *n*-type and *p*-type compounds, and the determination of acceptor and donor concentrations.

Interpretation of the measured electrical properties from a theoretical point of view will be attempted in the following sections; such an interpretation must be preceded by a brief discussion of the band structure and electrical properties of graphite itself.

3. Band Structure of Graphite

Graphite is classified as a semimetal (136). Its conduction and valence (or lower conduction) bands are separated by a small energy gap which vanishes in certain crystallographic directions where a slight overlap of the bands is, in fact, likely. Several investigators have in recent years analyzed the band structure of graphite and derived the electrical properties. Such analyses have occasionally been simplified by the approximation that interaction between adjacent planes is sufficiently weak to be neglected so that only a two-dimensional hexagonal network of carbon atoms has to be considered. Although most analyses have proceeded further and taken account of interplanar effects, the two-dimensional analysis is probably more applicable to concentrated lamellar compounds because the interplanar forces of graphite are completely altered by the insertion of foreign substances.

A two-dimensional theory of the band structure of graphite due to Wallace (133) predicts that the two bands are in contact for electron motion along six directions parallel to the layer planes. The electron population of the bands is such that at the absolute zero of temperature one band is completely filled, the other one essentially empty. At room temperature thermal excitation populates the conduction band by about 10^{-4} electrons per atom and the valence band by an equivalent number of holes which also contribute to the electrical conductivity. Because the density of states is very low near the top of the lower band, the conductivity will be increased considerably by any impurity or reactant which either adds (donor) or withdraws (acceptor) an appreciable number of electrons from the conduction bands.

4. *Resistivity*

The resistivity changes associated with electron transfers from donors or acceptors have been calculated (43) from the two-dimensional theory of Wallace. The experimental resistances of *n*-type and *p*-type lamellar compounds have been plotted in Figure 10 together with calculated values. The results at 25°C. agree reasonably well.

The theory predicts that the temperature dependence of the resistivity becomes more metallic if donor or acceptors are introduced. Single crystals of graphite show a metallic temperature dependence even in the absence of impurities; i.e., their resistance increases with temperature because, as the temperature is raised, the increase in carrier concentration is more than compensated by increased scatter-

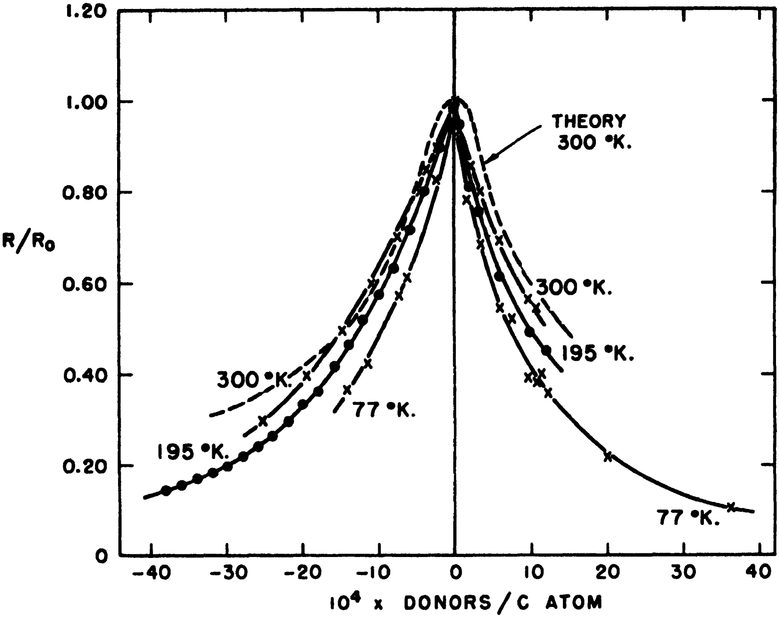

Fig. 10. Resistivities of graphite compounds measured at three temperatures and compared with theoretical values for 300°C. (44; reproduced with permission).

ing by thermal oscillations of the lattice. In polycrystalline graphite, this thermal scattering is masked up to about 400°C. by scattering from lattice imperfections and crystallite boundaries. This scattering by defects is temperature insensitive, so that the resistivity decreases with temperature. If donors or acceptors are added to artificial graphite, the effective number of carriers becomes progressively more independent of temperature, so that the only temperature dependence which remains is the relatively small lattice scattering which causes an increase in resistance with temperature.

The observed temperature dependence of the resistivity is thus explained qualitatively, but quantitative comparison with calculated values is not particularly satisfactory (43).

5. Hall Coefficients

The Hall effect is the electric potential which is measured on a sample perpendicular to a crossed electric and magnetic field. The sign of the Hall coefficient is an indication whether the effective concentration of positive (hole) or negative electrical carriers predominates. The two-dimensional theory outlined above predicts a zero value for the Hall effect of pure graphite except at very high temperatures because the assumptions in the theory result in symmetrical energy surfaces near the zone boundary. The predicted and measured Hall coefficients are plotted in Figure 11. Agreement between measured and predicted Hall values is quite poor. It could be improved considerably if the theoretical curve could be shifted as if pure graphite contained donor states and thus an excess of electrons over holes.

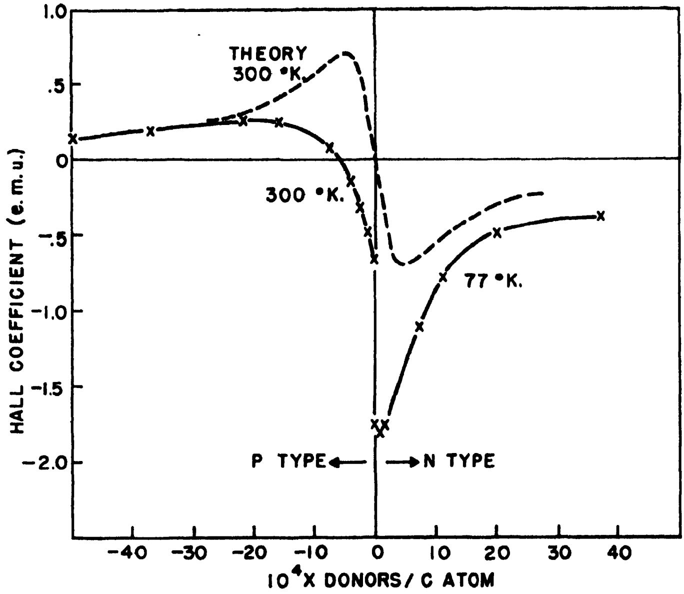

Fig. 11. Hall coefficients of lamellar compounds.

The poor agreement of the theoretical curve with Hall values even of pure graphite is due to inadequacies in the simplified theory used here. Actually, the two energy bands are probably not symmetrical so that the mobilities of holes and electrons are not equal. The possibility that in pure graphite the electron concentration exceeds the hole concentration has not been completely settled as yet even by more refined theories of three-dimensional energy bands of graphite (12,39,65,77,84).

6. Susceptibilities

The magnetic susceptibility of graphite has also been calculated from the simplified theory of two-dimensional bands (47,119). Graphite possesses a large diamagnetic susceptibility because the electrons in nearly empty bands behave as if their "effective mass" were abnormally small. As these electrons are removed by acceptors, the abnormal diamagnetism disappears. The same abnormal effective mass is also responsible for a large magneto resistance. This property is similarly observed to be decreased both by acceptors and by donors which populate the conduction band sufficiently that most of the electrons have more nearly normal "effective masses."

The calculated susceptibilities essentially agree with the single measurement reported by Goldsmith (34) on lamellar graphite bromide. The dependence of the susceptibility of graphite bromide on concentration was measured by Juza and co-workers (66) and is reported in Table X. Quantitative comparison with calculated susceptibilities has not been carried out because compounds prepared by Juza are not well-defined lamellar compounds, but are inter-

TABLE X
Relative Susceptibilities, χ/χ_0, of Lamellar Graphite Bromide (66) and Bisulfate (86)

Atom ratio Br/C, × 10^2	χ/χ_0	HSO_4^-/C, × 10^4	χ/χ_0
0	1.0	0	1.0
1.68	0.775	5	0.91
2.13	0.682	10	0.82
2.98	0.640	15	0.71
3.33	0.515		
3.57	0.460		
4.57	0.380		
4.72	0.396		
4.95	0.452		
4.98	0.415		
6.92	0.254		
7.06	0.185		
7.92	0.177		
8.25	0.098		
8.55	0.128		
12.5	0.043		

mediate in composition between lamellar and residue compounds, as explained earlier. Susceptibilities have also been reported for bisulfate compounds prepared from carbon heat treated at 2800°C. These measurements by Pinnick and Kiive (86) have been included in Table X.

Magnetic susceptibilities of several *p*-type compounds formed by metal halides have apparently been measured but not yet been published. Croft (22) reported the diamagnetism of graphite unchanged in some compounds, while Rudorff (98) observed the decrease of this diamagnetism expected for ionic compounds.

The contribution of the reactant to the total susceptibility of a lamellar compound is small only if the reactant is diamagnetic. Paramagnetic reactants overwhelm the susceptibility of graphite so that the compound is also paramagnetic. Potassium is weakly paramagnetic; the susceptibility of the potassium compound of graphite was shown by McDonnell, Pink, and Ubbelohde (78) to be considerably more paramagnetic than calculated by adding the contributions of potassium and carbon. The paramagnetism was, however, nearly temperature independent, analogous to the susceptibility of pure potassium, and could therefore not be accounted for by postulating the presence of isolated potassium atoms whose susceptibility would be inversely proportional to the temperature. Independent measurements of the alkali metal compounds by Rudorff and Schulze (105) yielded susceptibilities which showed a strong temperature dependence. Their values differed from those of Ubbelohde and coworkers, particularly at low temperatures. The temperature dependence reported by Rudorff and Schulze is opposite to the dependence expected for atomic potassium; as the temperature is lowered, the paramagnetism becomes smaller. No explanation for these properties has been advanced.

7. *Paramagnetic Resonance*

For a number of lamellar compounds, relatively intense and surprisingly narrow paramagnetic resonance absorptions near a *g* value of 2 have been reported (49,117). These resonances were attributed to the reactant or to carriers trapped at or near the reactant. The alternate explanation that these resonances are due to the electrical carriers themselves was rejected because some *p*-type and also some *n*-type compounds, e.g., ammonium compounds and graphite bromide do not manifest any resonances even though their carrier concentration is equal to the carrier population of compounds which show strong resonances. Recent unpublished work by Wagoner and Singer (132) on resonances in graphite single crystals free of chemical impurities has definitely identified such resonances as due to conduction electrons. In conjunction with previous observations (46) on less perfect crystals these measurements imply that the resonance may be masked by surface imperfections of the crystals. It is therefore not inconceivable that the resonances observed in the lamellar compounds are actually due to the carriers and that the differences in line width and apparent absence of absorption in some compounds are due to surface effects.

8. Ferric Chloride Compounds

The electrical properties of lamellar compounds of ferric chloride were found by us (28) to confirm an ionic structure $C_n^+ \cdot FeCl_3^- \cdot 3FeCl_3$. The measurements and their interpretation disagree with earlier determinations of conductivities and susceptibilities by Rudorff and Schulz (104). They reported only slight increases relative to graphite in the conductivities of the $C_{12}FeCl_3$ compound, a somewhat higher, two- to four-fold, increase for the $C_{36}FeCl_3$ compound, and a nearly twenty-fold decrease in conductivity for compounds more concentrated than $C_{10}FeCl_3$.

The disagreement must be resolved before the proposed generalization (46) that all lamellar compounds are ionic can be verified. The differences in the reported conductivities might well be attributed to differences in composition; our measurements applied only to dilute compounds, while the earlier results were obtained only on concentrated compounds. It is conceivable, but very unlikely, that the electron transfer which increases the conductivity occurs only in dilute but not in concentrated compounds. More probably, the disagreement is to be attributed to differences in methods. Rudorff and Schulze measured powder compacts under pressure, while we measured compounds prepared from rods of artificial graphite. The specific resistance of powder compacts of graphite even under several hundred atmospheres of pressure is about a hundred times higher than the resistivity of rod samples. We feel that this high resistance may have masked the effect of ferric chloride, particularly since most of the compounds tested as powders were "incomplete" and probably were relatively free of ferric chloride in the important peripheral particle surfaces. This interpretation of the different results is highly tentative. A crucial experiment should be performed in which the resistance of a single crystal is measured at progressively higher ferric chloride contents.

The susceptibilities of several lamellar ferric chloride compounds reported in Table XI were measured by Rudorff and Schulz. To decide whether these values are compatible with an electron transfer which was shown by resistivity and Hall measurements of dilute compounds to reduce one-fourth of the ferric chloride, the susceptibilities for such an ionic model of the compounds have been calculated. The small diamagnetic contributions from the carbon atom cores have been neglected in this calculation. The values for a molecular model were calculated by adding the full diamagnetic contribution of graphite to the paramagnetism of ferric chloride.

TABLE XI
Measured and Calculated Susceptibilities
of Lamellar Ferric Chloride Compounds

Mole ratio, C/$FeCl_3$	Temp., °K.	Measured χ_g (104)	Calculated χ_g	
			Ionic	Molecular
6.84	293	59.4	55.0	54.5
6.84	195	91.3	86.0	85.1
6.84	90	219.2	201	187.8
10.42	293	49.3	47	45.7
10.42	195	76.0	73.2	71.7
10.42	90	190.2	171	159.2
30.3	293	25.9	25.5	22.7
30.3	195	39.7	39.8	36 4
30.3	90	98.3	93.1	83.7

Agreement of the results with either model is poor. The disagreement is probably in part due to hydrolysis (20) of a small fraction of the ferric chloride to ferric hydroxide, which may have a very high specific susceptibility (134). Rudorff has pointed out that the calculated molecular data can be explained by assuming that the Weiss constant of ferric chloride is changed from −3 to +20 degrees in the compounds. In the author's opinion, the results of susceptibility determinations are not sufficiently definite to confirm either of the two models for the ferric chloride compound.

It can be concluded that the properties of ferric chloride compounds do not constitute a serious contradiction to the ionic model of lamellar compounds.

L. BONDING OF LAMELLAR COMPOUNDS

The ionic nature of the bonding in lamellar compounds appears to us to be rather well established by the results of electrical measurements. However, several models involving nonionic bond types have been proposed and will be discussed. Also, several investigators have suggested that an understanding of the bonding in lamellar compounds could be furthered by searching for analogous substances which manifest similar structures or properties as graphite compounds.

1. *Analogues*

A superficial structural similarity appears to exist between lamellar compounds and the ferrocene type (sandwich) compounds described in the first chapter of this volume. Numerous differences (22) exist, however, in optical, electrical, and magnetic properties which indicate that the bonding is entirely different. Ubbelohde (130) has emphasized the similarity of the alkali metal lamellar compounds to the addition compounds of alkali metals and several aromatic hydrocarbons. He also pointed out some outstanding differences in stoichiometry and reactivity, particularly differences in reactivity to sodium.

Croft (23) has shown that several laminar substances other than graphite show reactivities which appear analogous to the lamellar reaction of graphite. Boron nitride was reported to interact with a number of substances to form lamellar type compounds. AlB_2 and $CrCl_3$, which possess layer lattice structures, also seemed to form analogous compounds.

The lamellar reactions of boron nitride have more recently been disputed by Rudorff and Stumpp (109), who failed to obtain any X-ray evidence for such reactions. They attribute the results reported by Croft to impurities in his boron nitride, which was not white, as pure BN is, but black and lustrous.

2. Nonionic Bonding

Numerous models have been proposed which attribute the bonding in lamellar compounds to bond types different from ionic bonds.

Before extensive electrical measurements had been carried out, it was believed that different lamellar compounds could manifest a variety of bond types. The electrolytic lamellar compounds were nearly always considered to be ionic and were actually designated as graphite salts, but the bromine or ferric chloride compounds were deemed van der Waals' type, and others were believed to be covalent. As a consequence, the nonconducting compounds, graphite oxide and graphite fluoride, were frequently included among the lamellar compounds.

A type of bonding different from either van der Waals' or ionic bonding was suggested by McDonnell, Pink, and Ubbelohde (78) for some lamellar compounds. The bonds were considered to be pseudometallic linkages; however, support for such bonding was based on erroneous values of the identity periods, as Rudorff (105) has recently pointed out. Actually, metallic bonding appears contradicted by the spacings observed in these compounds.

A bond type which appears to be approximately covalent was suggested by Croft (22) for at least the lamellar halide compounds of Group IIIA metals, viz., BCl_3, $AlCl_3$, $GaCl_3$, $InCl_3$, $ThCl_3$, and YCl_3. Croft assumed a bonding different from ionic for these compounds because at least some of them, particularly aluminum chloride, cannot be reduced to stable divalent or univalent halides. For the aluminum chloride compound this postulate was shown by Dzurus and Hennig (28) to be incorrect. Very pure aluminum chloride does not react with graphite. Only in the presence of oxidizing agents, chlorine, iodine, ferric chloride, or others, can a ternary compound containing $AlCl_3$ be formed, which was shown by electrical measurements to be a *p*-type ionic compound. A lamellar compound containing only aluminum chloride and graphite, which was reported by Rudorff (110), was later also found (102) to contain chlorine in the same ratio as found by Dzurus (28).

The reaction of boron trichloride with graphite has very recently been re-examined by Rudorff (98) who failed to obtain any evidence for the reaction reported by Croft. No careful re-examination of the yttrium trichloride compound has as yet been carried out, but it seems unlikely that this substance forms a truly exceptional lamellar compound.

3. *Ionic Bonding*

The possibility of ionic bonding in lamellar compounds other than the electrolytic compounds had been considered repeatedly before electronic properties had been measured extensively. However, such considerations usually neglected the possibility that only a definite fraction of the reactant is ionized. Complete ionization of the reactant was found to be incompatible with measured properties such as the susceptibility of the ferric chloride compound, the space requirement of bromide ions (94), etc. The possibility of partially ionic bonding appears to have been suggested first by Rudorff (98). Although most lamellar compounds are now believed to be formed by an electron transfer mechanism, the degree to which this ionized reactant remains ionic is still subject to controversy. The Hall measurements (43) in particular have shown without doubt that the electron population of the conduction band is altered in all lamellar compounds. If the acceptors or donors did not remain ionic, but rather formed a covalent bond (34) to the carbon layer planes, it seems very unlikely that the planar structure of the carbon layer could be preserved. In fact, such covalent bonds are presumably formed in the nonconducting compounds of graphite with the results that the carbon atoms become tetrahedral, the layers buckle, and the electrical resistivity is increased enormously.

In our opinion, the available evidence favors a model for lamellar compounds which embodies only completely ionic plus van der Waals' bonds between reactants and graphite. Such a model can be utilized with some success in calculating the energy (and therefore also the stability and its concentration dependence) of lamellar compounds (46). The model also makes it possible to explain some of the differences in stability among different lamellar compounds. Qualitative considerations of this kind are very promising. The energy of lamellar compounds should depend on the difference between the work function of graphite and the electron affinity, or work function, of the reactant. Indeed, the alkali metals form progressively more stable compounds the lower the ionization potential of the metal. Lithium and sodium have relatively large ionization potentials and probably do not form concentrated compounds. The stability of the compounds is also favored by the electrostatic interaction of the ions which are formed. The stability is expected to be high if the charges of like sign are far separated and those of unlike sign are close together. As a consequence, the more dilute compounds are more stable than the concentrated ones. Also, spatial separation of like charges on the reactant is insured by the nonionized reactant atoms or molecules, which are always present. The nonionized species act as a sort of spacer between ions of like charge. A spacer is a more effective dielectric the higher its polarizability. It is probably this spacer requirement which renders $AlCl_3$ and NH_3 such effective stabilizers in ternary lamellar compounds. Probably the same spacer requirement permits sodium to enter graphite in combination with cesium (51).

4. *Energy of Formation*

A quantitative evaluation of the stabilities of lamellar compounds is based on a Born-Haber type of cycle. A somewhat similar but more approximate calculation was carried out by Ubbelohde (78).

The derivation described here differs somewhat from the published account (46). Our original derivation was based upon the concept that the bromide compound which is known from electrical measurements to be $C_n^+(3.5Br_2)^-$ could be described as $C_n^+Br^- \cdot 3Br_2$ or $Cn^+ \cdot 2\, Br_2 \cdot Br_3^-$ where it was believed that the energy of the reaction

$$Br^- + Br_2 \rightarrow Br_3^- \tag{9}$$

was small. The calculated energies were not in reasonable agreement with experimental data. If one assumes, however, that the compound formation does not involve dissociation of bromine, and the compound is written as $C_n^+ \cdot Br_2^- \cdot 2.5Br_2$, much better results are obtained. The energies are calculated for the quantity of compound which contains one mole of bromide ion. For reasons discussed in Section III-I-2, the reactants are chosen as solids, e.g., Br_2 (solid) and graphite C_n. The over-all reaction is analyzed as the sum of two hypothetical consecutive reactions. The first reaction is the insertion of nonionized bromine layers into appropriate interlaminar spaces.

$$C_n + {}^7/_2Br_2\,(s) \rightarrow C_n \cdot {}^7/_2Br_2 \tag{10}$$

The energy change, U_0, is probably positive; it involves van der Waals' terms, including the rearrangement of the bromine lattice to fit the more loosely packed interlaminar arrangement.

The second partial reaction is the transfer of electrons from the carbon layers to bromine atoms.

$$C_n \cdot 3.5\, Br_2 \rightarrow C_n^+ \cdot Br_2^- \cdot 2.5\, Br_2 \tag{11}$$

$$\Delta E_{11} = W - A + P - \sum_n \Delta_a - U_0 + U \tag{12}$$

The energy requirements include the difference in the work function, W, of graphite minus the electron affinity, A, of molecular bromine, and the electrostatic energy, P, of the resulting ionic array. Furthermore, the van der Waals' energy, U_0, will be altered slightly and become U because part of the Br_2 molecules are replaced by Br_2^- ions. The work function, W, is not constant, but increases as progressively more electrons are removed from the graphite conduction band, because the top of the electron "sea," i.e., the Fermi energy, is lowered by removal of electrons. For every electron removed, this Fermi energy is lowered by an amount Δ_a, which can be calculated from various band models. For the two-dimensional band model of Wallace, $\Delta_a = (4.4m)^{1/2}$ e.v. at low temperatures, and m is the concentration of acceptors per carbon atom. Values of A, the electron affinity of molecular bromine, are not known. The assumption will be made here that A is equal to the electron affinity of atomic bromine.

The energy requirement of the reaction is obtained by adding the contributions of the two partial reactions. The free energy change differs from this quantity principally by the entropy of reaction. The assumption will be made that this entropy term is negligible because the reaction product is highly ordered, or that it is at least insensitive to the concentration of the lamellar compound and the chemical species of the reactant. These assumptions concerning the entropy require experimental confirmation. For n-type compounds, the expression contains several different terms. Δ_a is replaced by Δ_d, and the electron affinity, A, is replaced by the ionization potential, I:

$$\Delta F = -W + I + U + P + \sum_n \Delta_d \tag{13}$$

These relations for the free energy of formation will be used in the following sections to estimate the concentration dependence and the dependence of the stability on the reactant species. These experimental values pertain to partial molar free energies, $\overline{\Delta F}$, which are obtained from the expression (13) by omitting the summation sign, $\sum_n$, in the last term.

It should be noted that a resonance energy term ought to be included if the charge is really free to move between the molecules or atoms of the reactant. The calculation of this term seems to be a challenging theoretical problem.

5. Concentration Dependence

The expression for the free energy of lamellar compounds can be compared with experimental values, derived in Section III-I-2 from the vapor pressures of the reactant in equilibrium with the lamellar compounds. Since only P and Δ in equations 12 and 13 are likely to be concentration dependent, one may write

$$\overline{\Delta F} = B + P \pm \Delta \tag{14}$$

where B contains the terms which are not concentration dependent. For dilute graphite bromide compounds the value Δ, calculated from the two-dimensional model of Wallace for the energy contour of the conduction band, agrees fairly well with measured values of the pressure dependence as shown by Hennig and McClelland (47). Apparently the electrostatic term, P, is essentially independent of concentration in the dilute compound. Even at high concentration the electrostatic energy, P, was not found (46) to be very dependent on concentration. A theoretical evaluation of the electrostatic energy and its concentration dependence is very difficult principally because the effective dielectric constant, and therefore the distribution of the positive charge on the carbon layers, are not known. Several limiting cases have been considered. If the charge is localized entirely on the carbon layers adjacent to each reactant layer, P and also Δ would be independent of concentration; thus the vapor pressure would not change with concentration. This situation is obviously unrealistic. If the charge on the carbon is always uniformly distributed on all carbon layers, not only is the estimated electrostatic energy highly concentration dependent but it also diverges for dilute compounds, again an unrealistic solution. The correct distribution is probably a compromise between these extremes. The charge on the carbon is somewhat but not completely localized near the reactant layers and the distribution alters with concentration, presumably because the effective dielectric constants change.

The characteristic changes in slope of the free energy curves occurring at concentrations corresponding to definite stages of the potassium and the bisulfate compounds are also not clearly implied in equations 12 and 13. Some justification (46) has been reported for attributing these changes in slope to Δ, but they may also be caused by the neglected entropy of the compounds which may contribute to the less ordered compounds containing simultaneously two stages. The changes in slope may even indicate that two separate phases are present.

6. *Relative Stability of Different Compounds*

The relative stability of different compounds can be estimated from equation 13. If compounds of equal concentration stage and equal ion concentration are compared, differences among different

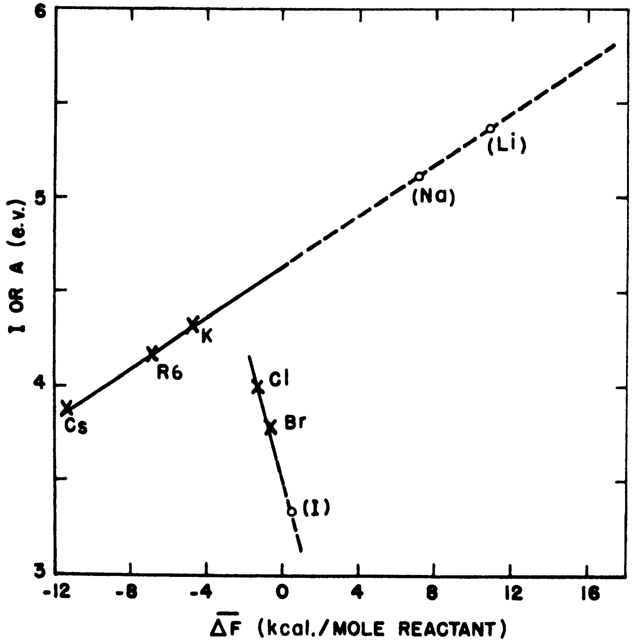

Fig. 12. Dependence of partial molar free energies on ionization potentials or electron affinities.

reactants will be predominantly due to different values of I or A. For instance, for several alkali metal compounds, the free energy, $\Delta\bar{F}$, is expected to be a function mainly of I. Figure 12 shows a plot of I against the experimental partial molar free energies calculated from the equilibrium pressures. The results define a straight line, which can be extrapolated to values of I for sodium and lithium and shows that for these substances the free energy is positive; i.e., concentrated compounds of these compounds are unstable. Similarly, the partial molar free energies of halogen compounds at concentrations $C_{12}X$, plotted in Figure 12 against the electron affinity, A, extrapolate to a positive free energy for the iodine compound in agreement with the observation that this compound cannot be prepared.

7. *Lattice Energies*

Reasonable values for the lattice energy, $P + U_1$, can be calculated by substitution of experimental free energies into equations 12 and 13. The experimental values of the partial molar free energies taken from Figure 9 are reported in calories per mole of reactant. For substitution into equations 12 and 13 they have to be multiplied by 4 for the potassium compounds and by 3.5 for the bromides. At an ion concentration of 0.01, the values are -0.15 e.v. per ion for the bromide and -1.55 e.v. for the potassium compound. Other values required are $W = 4.56$ e.v., $A = 3.53$ e.v., and $I = 4.32$ e.v. The values of Δ_d and $-\Delta_a$ will be taken to be equal at 0.2 e.v. This value, calculated from $\Delta_a = (4.4m)^{1/2}$, is also in approximate agreement with energy contours reported for a three-dimensional graphite lattice by Coulson (18). From equations 12 and 13 one obtains for $P_a + U_1$, the lattice energy for graphite bromide, -1.38 e.v. The lattice energy of the potassium compound is -1.51 e.v. per mole of ions. It was anticipated that these two energies would be about equal because, except for reversal of sign, the ion lattices of the two compounds are believed to be very similar. The lattice energy of 1.5 e.v. is considerably lower than the lattice energies of alkali halides, which range from 6 to 10 e.v., but, since the ion concentration is also much lower in the lamellar compounds, the calculated value is not unreasonable.

8. *Metal Halide Compounds*

The free energy of formation of metal halide lamellar compounds can be expressed by a relation analogous to equations 12 and 13.

The formulation of this expression depends, however, on whether or not the compounds are assumed to contain molecular ions. Using as an example the ferric chloride compound, the partial molar free energy for $C_n{}^+Cl^- \cdot FeCl_2 \cdot 3FeCl_3$ is

$$\overline{\Delta F} = W + {}^1/_2D - A_1 - Q + U + P - \Delta_a \qquad (14)$$

where D is the heat of dissociation of the halogen, A_1 the electron affinity of halogen atoms, and Q the heat of reaction of $FeCl_2 + {}^1/_2 Cl_2 \rightarrow FeCl_3$. The partial molar free energy of the ferric chloride compound was estimated from equation 14 by substituting the same lattice energy ($P + U$), of -1.38 e.v., which had previously been evaluated for graphite bromide. A value of $\Delta\bar{F} = +1.16$ e.v. at an ion concentration of 0.01 was obtained. Since the compound is known to be stable at much higher concentrations, the assumptions leading to equation 14, in particular the assumption of unbonded halogen ions in the compounds, must be in error.

To evaluate the free energy for metal halide compounds assumed to contain molecular ions, e.g., $C_n{}^+FeCl_3{}^- \cdot 3\ FeCl_3$, one has to add to equation 14 the energy, E_2, for

$$Cl^- + FeCl_2 \rightarrow FeCl_3{}^- \qquad (15)$$

which cannot be evaluated from available data. An alternate correction of equation 14 involves omitting D, Q, and A_1 and adding the electron affinity, A_2, of the metal halide. This quantity A_2 also can not be evaluated from available data.

It must be concluded that calculations of relative stabilities of metal halide lamellar compounds are at the present time not possible. The experimental determination of electron affinities, A_2, for gaseous metal halides does not appear an excessively difficult problem. It is hoped that such values may become available, so that one may attempt to calculate stabilities of metal halide lamellar compounds.

M. DOUBTFUL LAMELLAR COMPOUNDS

It was shown that the stability or instability of certain crucial lamellar compounds is predicted from theories of bonding in lamellar compounds. The formation of these compounds has been attempted repeatedly as will be described.

1. *Iodine Compounds*

Several investigators have reported that iodine does not react with graphite. For reasons outlined earlier, we felt that at least dilute compounds should be formed, but failed to obtain any evidence for these even after reacting for several months or at elevated pressures (50). The possibility was considered that reaction of iodine is prevented by some surface barrier on the graphite crystals. Tests were therefore conducted in which the crystals were pretreated in various gases or burned extensively to alter the surface. Even after such pretreatments, graphite failed to react with pure iodine.

2. *Sodium Compounds*

Several authors (28,32) have reported that sodium does not react with graphite below 450°C. and reacts above this temperature only to form carbides (19) and not lamellar compounds. However, a dilute sodium compound, $C_{66}Na$, was recently reported by Asher and Wilson (2). Miss Dzurus in our laboratory has made extensive efforts to prepare these compounds and found that impurities, particularly oxygen, facilitated the entry of sodium into graphite, probably because Na_2O acts as a spacer or catalyst. We have not been able to prepare the compounds of Asher and Wilson from pure sodium and degassed graphite in very pure helium or *in vacuo*, presumably because the required catalysts had been removed (50).

3. *Lithium Compounds*

Evidence was reported by Herold (51) that lithium reacts with graphite to form a compound C_4Li. It was not stated whether the lithium was sufficiently free of potassium so that its reaction did not mask the reaction of lithium. X-ray data were not obtained on the compound. The reaction apparently did not proceed uniformly but only attacked some of the crystals present. It is hoped that this compound will be studied further because if its existence can really be proved, some of the foregoing conclusions will have to be revised.

4. *Hydrogen Compounds*

The data of Figure 12 suggest that hydrogen should form a *p*-type lamellar compound with graphite. However, it seems unlikely that such a compound can be prepared at or above room temperature because of the energy terms of equation 8. At the more favorable temperature of boiling hydrogen the reaction may be extremely slow. Nevertheless, reactions of hydrogen with graphite have been investigated at and above room temperature, utilizing sensitive electrical properties as a test for compound formation. Evidence for spontaneous reaction was not found (50). However, relatively large amounts of hydrogen can be forced into graphite by a direct current discharge. Montet (80) has found that hydrogen introduced into graphite by a discharge is released by heating and that an appreciable fraction is released as hydrocarbons. The effect of hydrogen on the electrical properties of graphite has not yet been determined. Chaberski (13) reported an effect of hydrogen on the Hall coefficient of partly graphitized carbon.

IV. Residue Compounds

A. PREPARATION

It has been noted by many investigators that most lamellar compounds cannot be decomposed completely under ordinary conditions. While most of the reactant can be driven off at temperatures not very much higher than the temperature of formation, a significant residue is retained much more tenaciously. Investigation of this retention of a residue from lamellar compounds showed that the retention was not merely an accidental and unpredictable contamination, but was, in fact, reproducible for a particular type of graphite, reactant, and concentration of lamellar compound. In artificial polycrystalline graphites approximately two-thirds of the lamellar reactant is lost with relative ease; the remaining third is retained with extreme tenacity. Because of their predictability of composition and because of their characteristic properties which differ considerably from those of lamellar compounds, these decomposition products of lamellar compounds have been designated as residue compounds (44). Residue compounds can probably be prepared only from the corresponding lamellar compounds of graphite.

The composition of residue compounds depends very strongly on the type and perfection of the original graphite, whereas lamellar compounds are relatively (51) insensitive to such variables. Lamellar compounds prepared from large crystals of natural graphite usually decompose only slowly. However, the decomposition does not

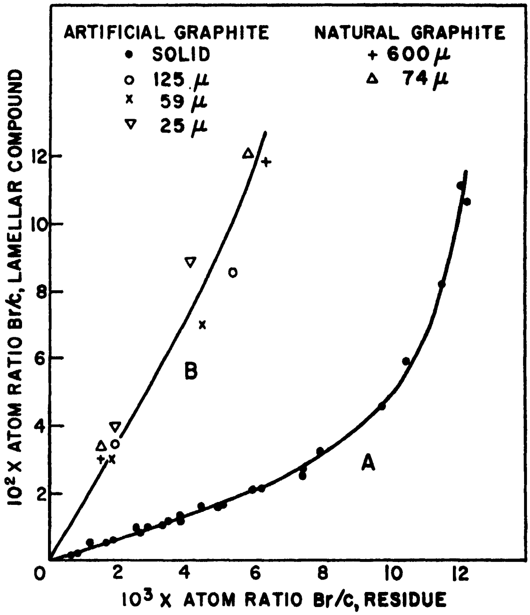

Fig. 13. Retention of bromine as a function of the composition of the parent lamellar compound, and the graphite type (44).

cease abruptly at some fixed composition; rather, it proceeds gradually to completion, particularly at elevated temperature. Therefore, for large crystals, one can hardly define actual residue compounds. For smaller crystals, and particularly for polycrystalline graphite, the decomposition of lamellar compounds is more rapid, but it ceases abruptly at the composition of the residue compound. As an example, curve *A* in Figure 13 shows the composition of graphite bromide residue compounds together with the compositions of the parent lamellar compounds prepared from rods of pitch bonded artificial graphite. The residue compounds were obtained simply by driving off the bromide at 50°C. Heating for two days at 350°C. decreased the composition of the residue compounds by less than 8% and heating to even 2000°C. did not remove the residual bromine completely. Curve *B* (Fig. 13) shows the composition of the residues obtained from powders of the same and of more perfect graphites after heating to 310°C. The retention in powders is obviously less complete than in solid rods. It is accidentally about equal for the various samples at a temperature of 310°C. At lower and at higher temperatures the retention values would be different for the different powders.

The formation of bromide residue compounds from graphites of different lattice perfection was studied in great detail by Maire and Mering (75). These authors confirmed that residue compounds are formed only by imperfect graphite using the value of the *c* spacing as an index of perfection. For graphites containing less than 75% graphitic layer spacings (3.35 A.) and more than 25% nongraphitic spacings (3.44 A.) the fraction of lamellar bromine retained as a residue compound at 350°C. was constant at about 20%. More completely graphitized samples retained less bromine. Completely graphitized material still retained a finite amount as a residue after heating to 350°C.; this was attributed to occlusion within large crystallites. Rudorff (98) has studied this occlusion of bromine within the crystallites of nearly perfect graphite and observed it to depend upon the rate of debromination, the crystallite size, and other variables, which seem to be less important in affecting the retention of bromine by imperfect graphites.

Lamellar graphite bisulfates can be reduced to residue compounds which show essentially the same concentration relation to the parent lamellar compounds as the bromides do. Although concentration relations have not been studied systematically for other compounds, approximately the same relations as in Figure 13 have been found for residue compounds of ferric chloride, uranium halides, chlorine–aluminum trichloride, alkali and alkaline earth amines, and electrolytic ammonium compounds.

Potassium does not form residue compounds even with artificial graphite. Its lamellar compounds decompose completely at the temperature of formation when the vapor pressure of the metal is reduced. Apparently potassium and probably also rubidium and cesium are unique in this respect, since no other lamellar compound has been reported which does not form residue compounds during decomposition.

B. STRUCTURE

There exists little doubt that residue compounds retain the reactant at crystal imperfections. Our original suggestion (44) attributed the retention to crystallite boundaries, mosaic boundaries, twin lines, and vacancies. The suggestion was based upon the observation that the residue did not increase the *c* spacing of graphite. Maire and Mering observed definite X-ray lines of bromine in bromide residue compounds which showed the asymmetry characteristic of two-dimensional layers. They suggested that single layers of bromine are retained at the interfaces between imperfect layer planes and perfect layer planes. Contacts between two imperfect layer planes, separated by 3.44 A., are not capable of admitting or retaining bromine, as shown by the fact that very poorly graphitized graphites do not react with bromine. Contacts between two perfect layer planes, separated by 3.35 A., admit but do not retain bromine. The occlusion of bromine by nearly perfect crystallites was shown by Rudorff (98) to result in the retention of the diffraction lines of three-dimensional lamellar graphite bromide with mere reduction in intensity.

C. PROPERTIES

In Section III-K-3 it was pointed out that the electrical properties of lamellar graphite compounds are difficult to correlate with the band structure of graphite because these compounds are ordered, possess a superlattice structure, and therefore distort the band structure of graphite to an unknown and probably variable extent. The residue compounds of graphite do not possess any characteristic structure and are therefore not likely to distort the band structure of graphite very considerably. The electrical properties of residue compounds are therefore of particular interest. They have been interpreted in terms of refined conduction band theories derived for graphite (60,62,43).

Such a use of the electrical properties of residue compounds requires a knowledge of the acceptor or donor concentration in each compound, i.e., a knowledge of the extent of ionization of the known amount of reactant present. Obviously, the total amount of reactant present can be obtained by weighing, since most residue compounds are entirely stable to washing or even moderate heating. The determination of the ion concentration requires calibration with an electrolytic compound for which the acceptor or donor concentration is determined electrolytically.

This electrolytic determination is carried out by measuring the current required to convert the residue compound into a lamellar compound of known resistance and ion concentration. This process proceeds at unit current efficiency (43). The direct determination of ion concentrations by measuring the current required to convert the original lamellar compound into its residue compound has been shown (29,43) to be unreliable because some of the current in this conversion is apparently diverted to a parasitic reaction, possibly evolution of hydrogen or oxygen.

In nonelectrolytic residue compounds the ion concentration is estimated from electrolytic compounds of equal resistivity or Hall coefficients. The assumption is made that the electrical properties of all residue compounds are equal at equal acceptor or donor concentrations. This assumption seems justified because for at least three different sets of residue compounds, i.e., the chloride, bromide, and bisulfate, agreement of any one electrical property, e.g., resistivity, also guarantees agreement of quite different properties such as Hall coefficient or magneto resistance.

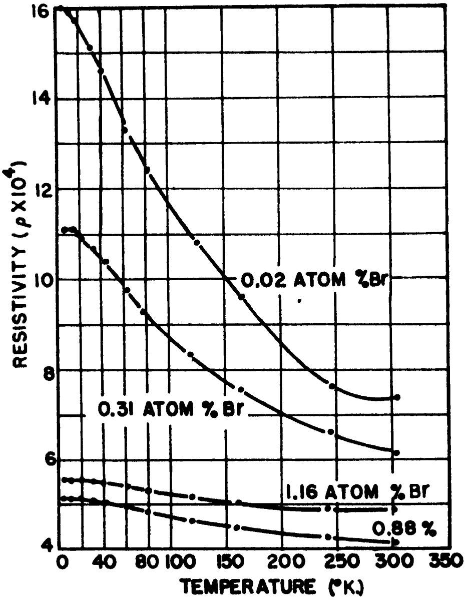

Fig. 14. Temperature dependence of the resistivity of graphite bromide residue compounds (118; reproduced with permission).

For compounds prepared from artificial graphite, electrical prop-

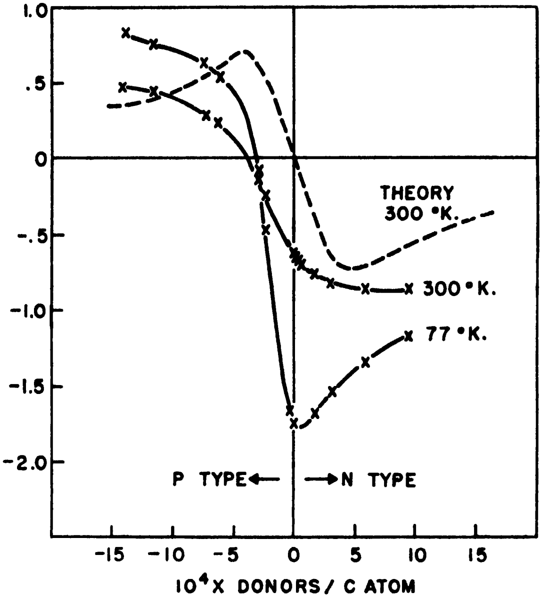

Fig. 15. Hall coefficients of residue compounds of graphite (29; reproduced with permission).

erties can only be measured up to an ion concentration of about 1.5 × 10^{-3} per carbon atom. At higher concentrations the compounds begin to disintegrate and yield unreliable values.

The resistivities of residue compounds were found to be equal to the resistivities of lamellar compounds of equal acceptor or donor concentration. They are therefore represented by Figure 10. The resistivities were incidentally measured to very low temperatures to search for superconductivity which was not observed in these compounds (48). The temperature dependence of the resistance is shown in Figure 14.

The Hall coefficients and magneto resistances are shown in Figures 15 and 16. The magnetic susceptibility has thus far been measured only for *p*-type compounds and is shown in Figure 17.

In spite of the qualitative agreement of the electrical properties with anticipated values, a quantitative interpretation of the properties is difficult. The difficulty is greatest for the resistances of residue compounds because these show a characteristic discontinuity in slope at low impurity concentrations and at all temperatures, which cannot readily be accounted for. Calculations of the resistance for various models of the graphitic band structure have been carried out in which the carrier concentration was computed for various acceptor or donor concentrations (29,43,80). Resistance was then calculated from the assumption that the mobility of the carriers was the same as in pure graphite. This assumption seemed justified (42) because the reactant is localized not within the graphite lattice where it could influence the carriers but at imperfections in the lattice which themselves lower the mobility of carriers even in the absence of the reactant. However, it was realized that this assumption of constant mobilities was at best an approximation (43,81). The data of Figure 10, particularly the discontinuous rate of resistance change at low impuritiy content, seem to suggest that the mobilities of the carriers are actually increased by

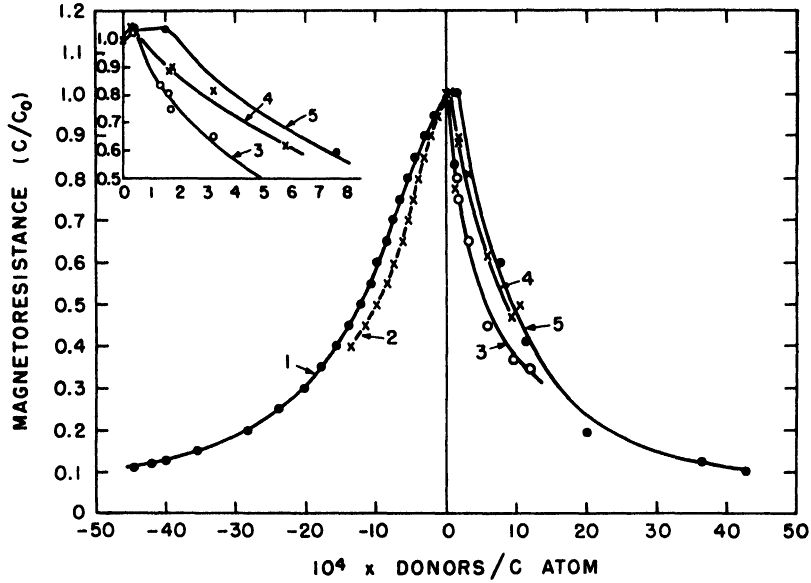

Fig. 16. Magnetoresistance of graphite compounds. *1*, lamellar compound at 300°K.; *2*, residue compound at 300°K.; *3*, residue compound at 77°K.; *4*, residue compound at 300°K.; *5*, lamellar compound at 77°K. The insert shows details of the region of low impurity concentration. For each temperature the magnetoresistance values C are reported relative to the values C_0 for pure graphite at 10 kg. (29; reproduced with permission).

impurities and possibly by altered intercrystalline contacts. An alternate or supplementary possibility of attributing the inexplicable resistance behavior to inhomogeneous distributions of the reactant in the residue compounds has been explored to some extent (29,42).

Other electrical properties of the residue compounds agree somewhat better with theoretical predictions, particularly those properties which are less sensitive to the carrier mobilities. Such comparisons are shown for the Hall coefficients and susceptibilities in Figures 15 and 17.

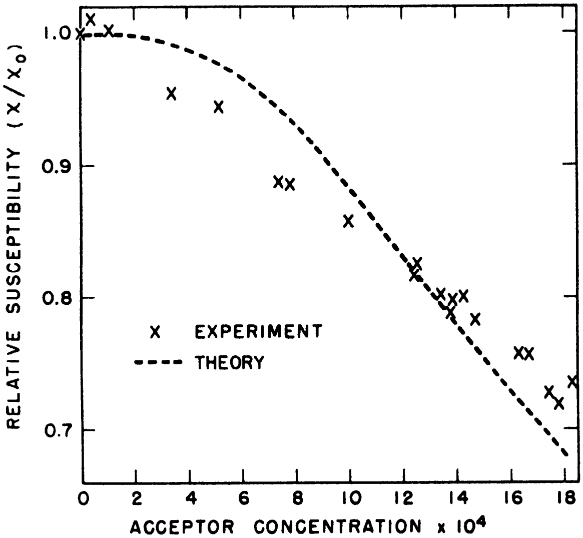

Fig. 17. Relative susceptibilities of residue compounds (47).

Thermal conductivities of bromide residue compounds were measured by Hove, Smith, and Rasor (63,118) and are shown in Figure 18. The thermal conductivity of graphite is almost entirely a lattice conductivity; the electrons and holes contribute only negligibly tc the conductivity. It was therefore anticipated that the conductivity of residue compounds which alter only the electron population should not differ from the conductivity of graphite itself. Actually a considerable reduction in conductivity by residual bromine was observed. Apparently the mean free path of phonons is considerably more sensitive than the mean free path of electrical carriers to the presence of

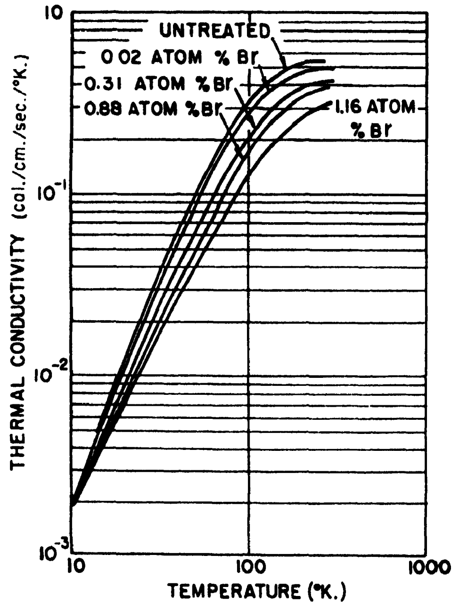

Fig. 18. Thermal conductivities of residue compounds (118; reproduced with permission).

residual bromine. The change in the temperature dependence of the conductivity, which was discussed in considerable detail by Hove and Smith (63), should also be noted.

D. COMPOSITION

Donor or acceptor concentrations were determined for many residue compounds by the method of comparing their electrical properties with those of electrolytic residue compounds as outlined in Section III-K-2. The measurements have shown that the fraction of the reactant which is ionized in the residue compounds is not the same as in lamellar compounds. In bisulfate residue compounds of a wide range of concentrations one-fifth of the sulfuric acid is ionized and is thus bisulfate ion, whereas in lamellar compounds one-third of the sulfuric acid is thus ionized. In residue bromide compounds two out of eleven bromine atoms are ionic as compared to one out of seven lamellar bromine atoms. No explanation has been advanced for these differences.

V. Applications of Interstitial Compounds

A. PRACTICAL USES

Numerous suggestions have been made for practical applications of interstitial compounds of graphite, but surprisingly few applications have come into use. Suggested uses include chemical separations, catalysis, oxidation inhibitors, electrode reactions, graphite synthesis, battery components, and semipermeable membranes.

The selectivity of lamellar compound formation has led to several suggestions for chemical separations. Actually, only the partial removal of potassium from sodium (79), the separation of some of the rare earth halides (131), and the separation of $AlCl_3$ and $FeCl_3$ (24) have been accomplished.

Lamellar compound formation has been suggested but not confirmed as an explanation for the ability of graphite to catalyze the formation of hydrogen bromide (98) or the bromination of hydrocarbons (50).

The ability of lamellar compounds to inhibit the oxidation of graphite appears to be implied in a model of oxidation catalyses proposed by Long and Sykes (72). According to this model, catalysts act by withdrawing electrons from the carbon bond system. Thus one would anticipate electron donors to inhibit the oxidation. We tested several lamellar compounds and found that some *n*-type and some *p*-type compounds, particularly the ferric chloride compound, burned much faster than graphite. It is known that halogens (41) inhibit the oxidation (135) of graphite. However, the inhibition can hardly be attributed to lamellar compound formation because the temperatures are far too high for compounds to be stable.

Certain lamellar reactions have been studied with a view of preventing the deterioration of electrodes used for electrolytic reactions. The conditions under which fluorides are capable of attacking graphite electrodes by forming lamellar compounds were discussed by Rudorff *et al.* (101).

Several uses are based upon the properties of graphite oxide. This substance has been used (31) on a laboratory scale in the synthesis of artificial graphites of special properties. Graphite oxide has also been tested and used (10) as a depolarizer in dry cells. It was claimed to excel manganese dioxide for some applications.

Semipermeable membranes have been prepared from graphite oxide by Clauss, Hofmann, and Weiss (14,15). These membranes were found useful for activity determination of ions in aqueous solutions. For most ions, reproducible potentials across the membrane were established in less than an hour. Some large ions, such as the alkaloids, required much longer times. However, trivalent ions like lanthanum did not yield reproducible potentials. Membranes of graphite oxide showed another startling property. When prepared carefully they were nearly impervious to gases like nitrogen and oxygen but at the same time allowed rapid diffusion of water vapor. They could therefore be used for direct measurements of partial pressures of water vapor. Since the membranes are known to absorb polar organic liquids, dioxane, acetone, etc., they are expected to be permeable to these vapors also.

B. APPLICATION IN RESEARCH

Interstitial compounds of graphite have frequently been used as analytical tools or as models in the study of reaction mechanisms, of graphitization reactions, of radiation damage, and of structural characteristics of graphite.

Probably the first use ever proposed for interstitial compounds concerned the distinction between carbons and graphites. Berthelot (6) claimed in 1870 that the formation of graphite oxide was a unique property of graphite which distinguished it from amorphous carbons. Later work (3) indicated that carbons are not always incapable of forming graphite oxide. Maire (73) showed that the formation of such oxides served to distinguish graphitizable from nongraphitizable carbons.

The formation of lamellar compounds has been used repeatedly to study the graphitization reaction. Mrozowski (68,81,86) and coworkers have studied the electrical properties of electrolytic compounds derived from carbons at various stages of graphitization. Mering (75), used the bromination reaction and the retention of residual bromine as an analytical tool for estimating the extent of graphitization. Platzer (87) has studied reactions of potassium with ungraphitized carbons.

Residue compounds of *p*-type graphite have been suggested as models (42) for radiation-damaged graphite because, in both, the conduction band of graphite is depleted by acceptor traps which are chemical impurities in *p*-type graphite and lattice defects in damaged graphite. The model differs from radiation-damaged graphite in the carrier mobility, which is altered but little in the residue compounds and altered considerably in the damaged graphite.

Lamellar and residue compounds have been prepared directly from radiation-damaged graphite (80). The reaction rates have been found to be decreased considerably by prior irradiation. The lamellar reactions actually eliminate part of the lattice defects produced by irradiation.

The elimination of radiation damage by lamellar reactions has been utilized for quantitative estimates of this damage. A considerable amount of energy (up to 600 cal. per gram) is stored in graphite during irradiation (82). The release of this energy by the lamellar reaction with potassium was studied by Primak and Quarterman (89,90). Unfortunately, neither all nor even a constant fraction of the stored energy is released in the reaction. Some of the displaced atoms apparently form carbides with potassium (88).

The estimation of the stored energy and free energy of radiation-damaged graphite from electrode potential measurements in sulfuric acid was attempted by us but failed to yield meaningful results (50).

Radiation damage in a lamellar compound was studied by Lazo and Hooley (71), who irradiated lamellar ferric chloride compounds and, by Szilard-Chalmers reactions, determined the ejection of iron from the compound, which they found to be insignificant.

VI. Summary and Conclusions

An effort has been made to present a critique as well as a review of interstitial compounds. Those ideas and experiments which have occasioned disagreement or controversies have been treated more exhaustively than others. As a consequence, the structural problems of interstitial compounds may have been discussed more briefly than their importance might warrant. Few disagreements have arisen concerning structural problems. In fact, recently published structures have in general tended to confirm the characteristics, particularly of lamellar compounds, which had already been established more than a decade ago and which have been reviewed repeatedly. In the discussions of electronic properties only the comparison with very simple calculated band structures have been included. Correlations with more refined theoretical calculations have been deemed outside the scope of this review and have only been mentioned and documented.

Interstitial compounds have been classified according to bond type as nonconducting compounds, lamellar compounds, and residue compounds. Evidence has been presented that the reactant is held by covalent bonds in the nonconducting compounds. It has been demonstrated that in all lamellar compounds the reactant is held by ionic and van der Waals' bonds. The residue compounds are closely related to the lamellar compounds because some of their bonds are also ionic. However, the extreme thermal stability and the formation of volatile carbon compounds during eventual thermal decomposition of residue compounds suggest that part of the reactant in these substances may be bonded covalently.

There remains little doubt that at least part of the carbon skeleton of nonconducting compounds consists of buckled layers, although occasional regions containing coplanar carbon bonds may exist in at least one nonconducting compound, graphite oxide. This class of compounds is further characterized by a wide range of possible compositions rather than a definite stoichiometry.

The lamellar compounds are characterized by definite periodic sequences of reactant and carbon layers (at least in the concentrated compounds), by a number of concentration stages of definite stoichiometry, and by numerous common electronic properties. These electronic properties have been interpreted as evidence that in this class of compounds a definite fixed fraction, usually about one-third, of the reactant has acquired a positive or negative charge. In electrolytic lamellar compounds, this charge is probably localized on ions. In some of the spontaneous lamellar compounds, this charge may be shared equally among all the reactant molecules, and thus contribute to the electrical conductivity. However, this contribution is probably small since the electronic properties of lamellar compounds are in essential agreement with theories of the electronic structure of graphite.

The residue compounds are not characterized by a definite structure or by a definite stoichiometry. The reactant is believed to be present at lattice imperfections. As a consequence, residue compounds cannot be prepared from highly crystalline natural graphite.

An effort has been made to emphasize problems which require further study to complete our understanding of interstitial compounds of graphite. It is hoped that this review may stimulate interest in these unique substances.

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Über Schwefel-Stickstoff-Verbindungen

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Im Folgenden wird eine Gruppe von Schwefel-Stickstoff-Verbindungen beschrieben, von der einige Glieder schon sehr lange bekannt, andere dagegen erst in jüngster Zeit hergestellt worden sind. Schon in dem Briefwechsel zwischen Liebig und Woehler wird auf das Auftreten von intensiven und merkwürdigen Farben bei der Umsetzung zwischen Schwefelchloriden und Ammoniak hingewiesen. Die damals schon auffälligen Erscheinungen sind auf die Bildung von Schwefelnitriden zurückzuführen. Wenn im Folgenden einige der heute bekannten chemischen und physikalischen Eigenschaften der Schwefelnitride und ihrer Derivate beschrieben werden, so geschieht das vor allem, um unseren Blick wieder auf viele merkwürdige Erscheinungen zu lenken, die uns in dieser Gruppe von Verbindungen immer noch entgegentreten, die immer noch einer Erklärung bedürfen, und deren Deutung wahrscheinlich unsere Kenntnis vom Wesen der chemischen Bindung bei anorganischen Stoffen ganz allgemein bereichern dürfte.

Es ist lediglich eine kleine Auswahl von Schwefel-Stickstoff-Verbindungen beschrieben. Die Beschränkung auf die Nitride des Schwefels und deren direkte Abkömmlinge mit vorwiegend kovalenter Bindung zeigt aber deutlich das Charakteristische in diesem Gebiet der Chemie, von dem mir die Festigkeit der Bindung zwischen S und N, sowie die Tendenz zur Ausbildung acht- und sechsgliedriger Ringsysteme besonders bemerkenswert erscheint.

I. Schwefelnitride

Nitride des Schwefels sind schon lange bekannt; allerdings ist man sich über die Zusammensetzung und Einheitlichkeit der hergestellten Stoffe erst in neuerer Zeit völlig klar geworden. Heute können die Verbindungen $(SN)_2$, $(SN)_4$, $(SN)_x$, S_4N_2, $S_{15}N_2$ und $S_{16}N_2$ als gesichert angesehen werden. Wie bereits ein oberflächlicher Blick auf die Zusammensetzung der Verbindungen lehrt, haben die Stickstoff-Schwefel-Verbindungen noch nicht einmal formal Ähnlichkeit mit den Stickstoff-Sauerstoff-Verbindungen, und dieser Eindruck verstärkt sich noch, wenn man die chemischen und physikalischen Eigenschaften der Stoffe näher betrachtet. Dieser Befund ist sicherlich wesentlich dadurch bedingt, dass im Falle der Stickstoff-Sauerstoff-Verbindungen der Stickstoff der elektropositivere, im Falle der Stickstoff-Schwefel-Verbindungen aber der elektronegativere Verbindungspartner ist.

A. TETRASCHWEFEL-TETRANITRID

Das am längsten und am besten bekannte Schwefelnitrid ist Tetraschwefel-tetranitrid, S_4N_4. Es wurde zuerst 1835 von Gregory (1) als Produkt der Reaktion zwischen Ammoniak und Dischwefeldichlorid beobachtet. Aber erst 61 Jahre nach der Entdeckung der Verbindung konnte die Formel S_4N_4 für die Substanz aufgestellt (2) und gesichert werden.

Tetraschwefel-tetranitrid ist bei Raumtemperatur fest. Der Schmelzpunkt beträgt 178°. Es bildet hellorange monokline Kristalle der Klasse C_{2h} mit der Raumgruppe $P2_1/n$ (3). Die Substanz ist in Wasser unlöslich, in vielen organischen Lösungsmitteln dagegen gut löslich (4).

S_4N_4 ist ein endothermer Stoff mit einer Bildungsenthalpie von 128,8 Kcal./Mol, und dementsprechend kann die Verbindung bei raschem Erhitzen oder auf Stoss hin unter Detonation in die Elemente zerfallen.

Struktur und Konstitutionsformel von Tetraschwefel-tetranitrid sind Gegenstand zahlreicher Untersuchungen gewesen (5). Die Strukturuntersuchung von D. Clark hat das Problem wohl weitgehend gelöst. Danach muss man in dem festen Tetraschwefeltetranitrid Moleküle von S_4N_4 annehmen, von denen jeweils vier in der Elementarzelle enthalten sind. Wie es Figur 1 zeigt, bilden die 4 Schwefelatome ein Bisphenoid, während die vier Stickstoffatome in einer Ebene liegen und die Ecken eines Quadrates besetzen. Der Winkel am Stickstoff beträgt 115°, während der Winkel am Schwefel zu 102° gemessen wurde. Auffällig ist, dass Clark zwischen S und N einen Abstand von 1,60 A. gefunden hat. Dieser Abstand ist kleiner als nach den Radien für eine kovalente Einfachbindung zu erwarten wäre (1,74 A.), aber grösser als man ihn bei Vorhandensein einer Doppelbindung zwischen S und N voraussehen würde (1,54 A.). Noch bemerkenswerter ist, dass die S-Atome, die auf derselben Seite der durch die Stickstoffatome gebildeten Ebene liegen, sich bis auf einen Abstand von 2,58 A. nähern, während der Abstand von zwei S-Atomen, die über ein Stickstoffatom miteinander verbunden sind, 2,71 A. beträgt. Wenn man die van der Waalschen Radien von S betrachtet, so sollte man für S-Atome, die nicht miteinander verbunden sind, einen Abstand von 3,7 A. erwarten. Tatsächlich nähern sich benachbarte S_4N_4-Moleküle im Kristallgitter bis zu diesem zu erwartenden Abstand (6).

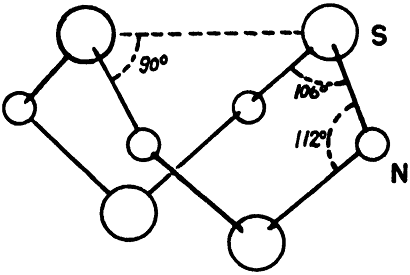
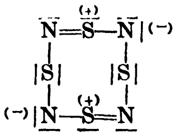
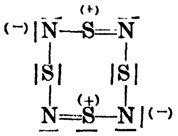
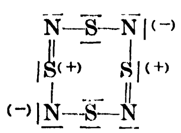


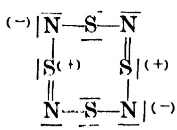
Fig. 1. Die Struktur des S_4N_4-Moleküls (nach Lu und Donohue).

Man kann die *Ergebnisse der Röntgenstrukturuntersuchung* in verschiedener Weise deuten. Von Lu und Donohue (7) und Clark (6) ist eine Mesomerie mit den Grenzformeln (Ia) bis (Ih) angenommen worden. Die durch diese Formeln zum Ausdruck kommende Resonanz würde gut erklären, warum der Abstand zwischen S und N geringer ist, als es für eine Einfachbindung zu erwarten wäre; denn diese Bindungen sollten ja einen erheblichen Doppelbindungsanteil besitzen. Auch die starke Annäherung der nicht über N miteinander verbundenen S-Atome lässt sich durch diese Grenzformeln deuten. Die chemischen Eigenschaften von S_4N_4 lassen sich ebenfalls durch diese Formeln deuten (8) und zwar so gut, dass Goehring (9) derartige Formeln vor Vorliegen der Strukturuntersuchung aus den chemischen Eigenschaften der Verbindung abgeleitet hat.


(Ia)


(Ib)


(Ic)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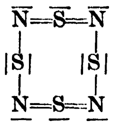
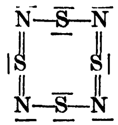
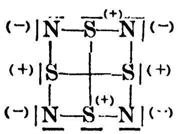
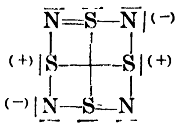

(Ie)


(If)


(Ig)


(Ih)

Lindqvist (10) hat eine interessante andere Deutung für die Ergebnisse der Strukturuntersuchung an S_4N_4 zur Diskussion gestellt. Er hat darauf hingewiesen, dass der Abstand zwischen zwei Atomen möglicherweise nicht nur eine Funktion der Bindungsordnung, d.h. des mehr oder weniger ausgeprägten Doppelbindungscharakters ist, sondern auch von dem *s*-Charakter der σ-Bindungen abhängt. Die Tatsache, dass der Schwefel-Schwefel-Abstand in $S_2O_6^{2-}$ mit 2,15 A. und in $S_2O_4^{2-}$ mit 2,39 A. grösser ist, als er für eine Einfachbindung zu erwarten wäre, lässt Lindqvist vermuten, dass in diesen Ionen die S–S-Bindung einen geringeren *s*-Charakter besitzt als z.B. im elementaren Schwefel S_8. S–S-Bindungen mit reinen *p*-Orbitals sollten danach noch länger sein, und es wäre dann denkbar, dass einer S–S-Bindung mit einem *s*-Charakter = 0 ein Abstand von 2,58 A. entspräche. Dieser Theorie würde Formel (Ig) gerecht werden.

Keine dieser Theorien deutet den Abstand von 2,71 A. zwischen zwei über ein N-Atom miteinander verbundenen S-Atomen, der ja ebenfalls viel kleiner ist als sich auf Grund der van der Waalschen Radien erwarten liesse.

Der Strukturuntersuchung von Clark (6) ging eine Elektronenbeugungsuntersuchung an S_4N_4-Dampf von Lu und Donohue (7) voraus. Sie hatte im Wesentlichen das gleiche Ergebnis wie die Arbeit von Clark, vgl. Tabelle I:

TABELLE I

Atomabstände und Bindungswinkel in S_4N_4

	Elektronenbeugung	Kristallstruktur
S–N Abstand (A.)	1,62	1,60
Bindungswinkel am N	112°	115°
Bindungswinkel am S	106°	102°

Eine zweite Untersuchung der Elektronenbeugung an S_4N_4 von Hassel und Viervoll (11) und ein Studium des Infrarot- und Ramanspektrums der Substanz von Lippincott und Tobin (12) hatten ein anderes Ergebnis, nach dem die Schwefelatome im S_4N_4-Molekül in einer Ebene liegen sollen und die N-Atome ein Bisphenoid bilden sollen. Worauf diese Diskrepanzen in den Strukturvorschlägen zurückzuführen sind, ist noch ungewiss. Es wäre erstaunlich, wenn man anzunehmen hätte, dass S_4N_4 im Dampfzustand und in Lösung eine andere Struktur besässe als im festen Zustand.

S_4N_4 bildet sich immer, wenn man in Lösungen von Schwefelchloriden wie SCl_2, S_2Cl_2 oder SCl_4 in indifferenten organischen Lösungsmitteln Ammoniak einleitet (13). Als Nebenprodukte entstehen NH_4Cl, Schwefel, S_7NH, und $S_6(NH)_2$. Weniger gut geeignet zur Herstellung von S_4N_4 ist die Disproportionierung, die elementarer Schwefel erleidet, wenn man ihn in verflüssigtem Ammoniak löst und diese Lösung auf Raumtemperatur erwärmt. Unter diesen Bedingungen entsteht aus dem Schwefel etwas H_2S und S_4N_4 (14) neben S_7NH (15).

Tetraschwefel-tetranitrid ist eine recht reaktionsfähige Substanz. Mit konzentrierter Jodwasserstoffsäure lässt sie sich zu H_2S und NH_3 reduzieren (16):

$$S_4N_4 + 20\,H^+ + 20\,I^- \longrightarrow 4\,H_2S + 4\,NH_3 + 10\,I_2$$

Mit starker Alkalilauge beobachtet man Hydrolyse nach:

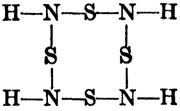
$$S_4N_4 + 6\,OH^- + 3\,H_2O \longrightarrow 2\,SO_3^{2-} + S_2O_3^{2-} + 4\,NH_3$$

Diese Reaktion (17) wird mit abnehmender Alkalikonzentration mehr und mehr überlagert durch die Umsetzung (9):

$$2\,S_4N_4 + 6\,OH^- + 9\,H_2O \longrightarrow 2\,S_3O_6^{2-} + S_2O_3^{2-} + 8\,NH_3$$

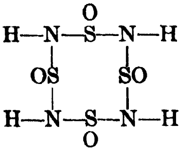
Durch vorsichtige Reduktion von S_4N_4 kann *Tetraschwefel-tetraimid*, $S_4(NH)_4$, hergestellt werden. Man reduziert zweckmässig eine benzolische Lösung von S_4N_4 mit einer methanolischen Lösung von $SnCl_2$ (18) oder eine methanolische Lösung von S_4N_4 mit $Na_2S_2O_4$. In beiden Fällen entsteht die Verbindung (II), die einen farblosen, kristallinen Stoff darstellt.

Tetraschwefel-tetraimid lässt sich leicht wieder zu S_4N_4 oxydieren. Behandelt man Lösungen von $S_4(NH)_4$ in der Kälte mit Chlor oder Brom, so entsteht S_4N_4, und noch glatter bildet sich dieses, wenn man (II) in ätherischer Suspension mit NO_2 umsetzt. Führt man die letztere Reaktion in der Hitze aus, so entsteht allerdings $[NO]_2S_2O_7$. Die Verbindung (II) lässt sich leicht weiter oxydieren. Erhitzt man sie—zweckmässig nach Verdünnen mit elementarem Schwefel—an der Luft auf 110° bis 120°, so bildet sich ein fester roter Stoff der Formel (III) (19).



(II)

Der Käfig des S_4N_4-Moleküls lässt sich also verhältnismässig leicht öffnen und in die achtgliedrigen Ringsysteme der Verbindungen (II) und (III) überführen. Die Struktur von (II) ist gut untersucht (20). Das Molekül stellt ein gewelltes achtgliedriges Ringsystem dar. Die vier S-Atome bilden ein Quadrat und die vier N-Atome bauen ebenfalls ein Quadrat auf, das in einer Ebene parallel zu der durch die S-Atome gebildeten Ebene liegt.



(III)

Eine analoge Verwandlung des aus acht Atomen aufgebauten Käfigs des S_4N_4-Moleküls in ein achtgliedriges Ringsystem findet offenbar statt, wenn man eine Lösung von Tetraschwefel-tetranitrid in Tetrachlorkohlenstoff mit AgF_2 reagieren lässt. Man kann durch diese Umsetzung weisses, festes $N_4S_4F_4$ (21) gewinnen. Aber schon bei dem Versuch der *Fluorierung* kann man bemerken, dass das achtgliedrige System des S_4N_4 leicht in kleinere Bruchstücke aufgespalten wird; denn beim Umsetzen von S_4N_4 mit AgF_2 in Tetrachlorkohlenstoff in der Hitze bildet sich farbloses gasförmiges SN_2F_2 (Fp −108°; Kp −11°) (V), aus dem durch thermische Zersetzung bei etwa 250° das ebenfalls farblose und gasförmige NSF (Fp −79°; Kp 4,8°) (VI) entsteht (22):

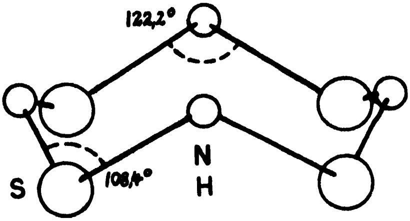
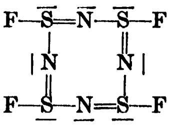


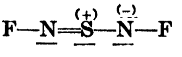
Fig. 2. Die Struktur des $S_4(NH)_4$-Moleküls.

$$2\,SN_2F_2 \longrightarrow 2\,NSF + F_2 + N_2$$

Zersetzt man SN_2F_2 unter milderen Bedingungen, dann bildet sich neben anderen Reaktionsprodukten und neben NSF auch SNF_3 (Fp −81°; Kp −23°) (VIII). Schliesslich kann bei der Reaktion zwischen S_4N_4 und AgF_2 im Gemisch mit der Verbindung (V) auch SNF erhalten werden, das ebenfalls gasförmig ist, und dem die Formel (VII) zugeschrieben wird (21).

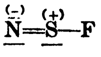


(IV)



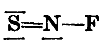
$$F{-}\underline{N}{=}\overset{(+)}{\underline{S}}{-}\overset{(-)}{\underline{N}}{-}F$$

(V)



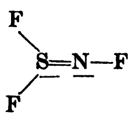
$$\overset{(-)}{\underline{N}}{=}\overset{(+)}{\underline{S}}{-}F$$

(VI)



$$\overline{\underline{S}}{=}\underline{N}{-}F$$

(VII)

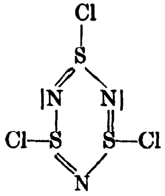


$$F_2S{=}\underline{N}{-}F$$

(VIII)

Eine Aufspaltung des zum Käfig zusammengebogenen Ringsystems des S_4N_4 wird ebenfalls beobachtet bei der *Reaktion mit Chlor oder mit Brom.* Behandelt man Tetraschwefel-tetranitrid in Chloroform-

oder in Tetrachlorkohlenstoff-Lösung mit Chlor, so erhält man eine wohlkristallisierte gelbe Substanz (23), deren Zusammensetzung und deren Molekulargewicht der Formel (IX) entspricht (24). Die



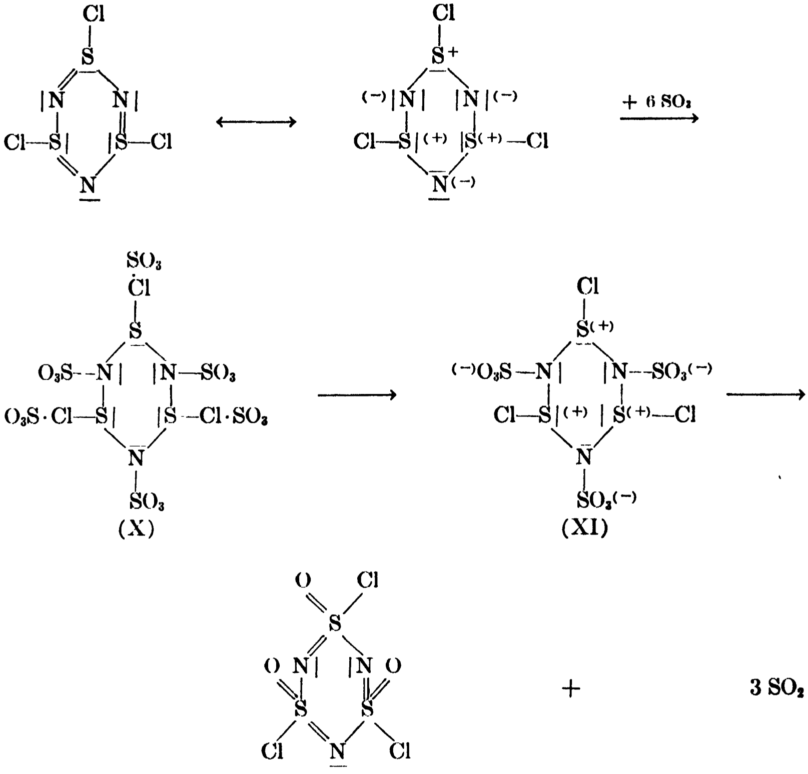
(IX)

Umsetzung mit Brom verläuft ganz analog. Aber die Brom-Verbindung ist in organischen Lösungsmitteln so wenig löslich, dass das Molekulargewicht bisher noch nicht bestimmt werden konnte. S_4N_4 und Brom liefern $[BrSN]_x$ (x vermutlich = 3). Bei der Umsetzung mit Chlor oder Brom wird offenbar das Gerüst des S_4N_4-Moleküls zerstört. Vermutlich bilden sich kleinere Bruchstücke—z.B. SN-Radikale—die dann halogeniert werden und sich schliesslich durch Trimerisierung zum sechsgliedrigen Ringsystem (IX) stabilisieren.

Die Verbindung (IX), die den Namen Trithiazylchlorid erhalten hat, kann ihrerseits sowohl unter Erhaltung des sechsgliedrigen Ringsystems wie auch unter Aufspaltung des Ringes mit anderen Stoffen weiter reagieren.

Unter Erhaltung des Ringsystems setzt sich Trithiazylchlorid mit Schwefeltrioxyd um. Die Verbindung addiert in der Kälte pro Mol 6 Mole SO_3 zu einem olivfarbigen Addukt, dem wahrscheinlich die Formel (X) zukommt. Die Hälfte des aufgenommenen Schwefeltrioxyds lässt sich entfernen, wenn man diesen Stoff im Vakuum auf etwa 50° erhitzt. Erhitzt man das so entstandene gelbe feste Addukt (XI) bei 20 torr auf etwa 150°, so entsteht Schwefeldioxyd und das farblose, feste *Sulfanurchlorid* (XII) (Fp 144–145°) (25,26). Diese Reaktion zeigt nicht nur, dass eine Oxydation des Ringsystems (IX) unter Erhaltung des Gerüstes möglich ist, sondern auch, dass Schwefeltrioxyd ein gutes Oxydationsmittel für Schwefel der Oxydationszahl +4 und der Koordinationszahl 3 darstellt.

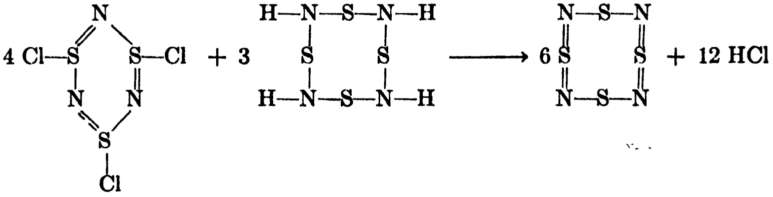
Während bei der vorsichtigen Oxydation das sechsgliedrige Ringsystem des Trithiazylchlorids erhalten bleibt, wird es schon bei der vorsichtigen Reduktion zerstört. Besonders interessant ist in dieser Hinsicht die Umsetzung mit Tetraschwefeltetraimid (II). Erhitzt



(X) (XI) (XII)

man (II) und (IX) in Tetrachlorkohlenstofflösung einige Zeit miteinander, so erhält man ein festes Reaktionsprodukt, das aus einem Gemisch von Thiotrithiazylchlorid, S_4N_3Cl, Tetraschwefel-tetranitrid, S_4N_4, und Ammoniumchlorid besteht.

Die Reaktion ist so zu deuten, dass zunächst aus $[ClSN]_3$ und $S_4(NH)_4$ Tetraschwefel-tetranitrid und HCl gebildet wird (26):



Wenn das entstandene HCl nicht durch Zusatz einer Base gebunden wird, wird es von S_4N_4 zu einem braunroten Addukt (XIII) addiert (27), und dieses vermag bei Anwesenheit von Spuren von Wasser zu Thiotrithiazylchlorid, Ammoniumchlorid, und Chlor zu reagieren:

$$\underset{\text{(XIII)}}{S_4N_4 \cdot 4\,HCl} \longrightarrow S_4N_3Cl + NH_4Cl + Cl_2$$

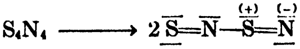
Aber diese Sekundärreaktion kann ganz zurückgedrängt werden, wenn man das HCl durch Zusatz von Pyridin bindet. In diesem Fall ist S_4N_4 neben Pyridiniumchlorid das einzige Reaktionsprodukt.

Gerade diese Reaktion zeigt, wie leicht in der Chemie der Schwefel-Stickstoff-Verbindungen die sechsgliedrigen und die achtgliedrigen Gerüstsysteme ineinander übergehen können.

B. DISCHWEFEL-DINITRID

Nicht nur durch chemische Reaktionen lässt sich das Gerüst des Tetraschwefel-tetranitrids zerstören und in andere stabile Systeme überführen; auch eine thermische Aufspaltung ist möglich. Dass S_4N_4 beim Erhitzen in die Elemente zerfallen kann, ist schon seit Entdeckung der Verbindung bekannt (vgl. Abt. I-A). Die erste Beobachtung, dass bei der thermischen Zersetzung auch flüchtige Schwefel-Stickstoff-Verbindungen entstehen können, machte Burt (28). Bei dem Versuch, S_4N_4 im Vakuum zu sublimieren, liess Burt S_4N_4-Dampf über ein Silberdrahtnetz und durch eine mit einem Dampfmantel erhitzte Zone streichen. Es schlug sich dann in der Apparatur ein blauer Film nieder, der seine Bildung nur einer flüchtigen, aus dem S_4N_4 entstandenen Schwefel-Stickstoff-Verbindung verdanken konnte. Die Zusammensetzung des blauen Filmes (29), die der Bruttoformel $(SN)_x$ entsprach, deutete darauf hin, dass aus S_4N_4 flüchtige Stoffe der gleichen Zusammensetzung aber von kleinerem Molekulargewicht entstanden sein mussten.

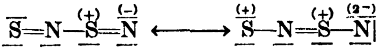
Goehring und Voigt (30) gelang dann die Zerlegung des S_4N_4-Moleküls bei gleichzeitiger Isolierung des Reaktionsproduktes, das tatsächlich die gleiche Zusammensetzung wie S_4N_4 aber ein kleineres Molekulargewicht hat. Dazu wurde S_4N_4 im Vakuum sublimiert, und der Dampf durch eine auf 300° erhitzte Zone geleitet, die mit Silberwolle, Kupfer- oder auch Quarzwolle gefüllt war. Bei dieser Arbeitsweise entstand aus S_4N_4 nur ganz wenig Schwefel und Stickstoff. Vorwiegend wurde ein flüchtiges Reaktionsprodukt gebildet, das in einer auf −80° gekühlten Falle kondensiert wurde, sich in organischen Lösungsmitteln wie z.B. Äther löste und aus diesen umkristallisiert werden konnte. Analyse und Molekulargewicht zeigte, dass dieser Substanz die Formel S_2N_2 zukommt.



$$S_4N_4 \longrightarrow 2\,\overline{\underline{S}}{=}\overline{N}{-}\overset{(+)}{\overline{S}}{=}\overset{(-)}{\overline{\underline{N}}}$$

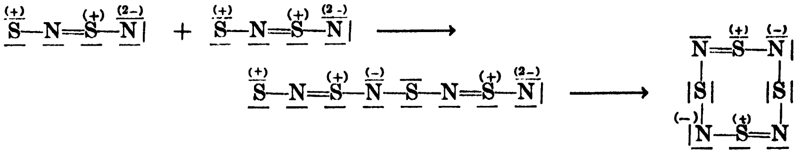
Dischwefel-dinitrid ist gut kristallisiert und farblos. Es ist flüchtig und sublimiert in einem Vakuum von 0,01 mm Hg schon bei Zimmertemperatur. Der Dampf besitzt einen sehr intensiven, wenig angenehmen Geruch. Bemerkenswert ist, dass die Substanz sich schon beim Erwärmen auf +30° explosionsartig zersetzt und Schwefel und elementaren Stickstoff bildet. Diese Zersetzung findet auch schon statt, wenn man die Substanz zu zerreiben versucht und ist von heftigen Detonationen begleitet.

S_2N_2 ist in vielen organischen Lösungsmitteln löslich, und diese Lösungen—z.B. die benzolische Lösung—sind beständiger als die feste Substanz. Gibt man zu einer derartigen Lösung von S_2N_2 eine Spur Alkalimetall oder ein Reagens wie z.B. Alkalikarbonat oder Alkalicyanid, so bildet sich rasch S_4N_4 aus dem S_2N_2 zurück. Diese Dimerisierung kann man aus der Formel (XIV) des S_2N_2 leicht verstehen. Es findet zunächst eine einfache Zusammenlagerung von zwei Molekülen statt, und dieses Zwischenprodukt vermag sich durch Aufbau des Ringsystems des S_4N_4 zu stabilisieren:



$$\overline{\underline{S}}{=}\underline{N}{-}\overset{(+)}{\underline{S}}{=}\overset{(-)}{\overline{\underline{N}}} \longleftrightarrow \overset{(+)}{\underline{S}}{-}\underline{N}{=}\overset{(+)}{\underline{S}}{-}\overset{(2-)}{\overline{\underline{N}}}|$$

(XIVa) (XIVb)



Anders verläuft die Polymerisation von S_2N_2, wenn man den Stoff unterhalb von +30° einfach einige Zeit sich selbst überlässt. Schliesst man dabei Luftfeuchtigkeit nicht aus, so beobachtet man, dass nach einigen Tagen der Geruch nach S_2N_2 verschwindet. Wieder kann S_4N_4 nachgewiesen werden; aber ausserdem entsteht noch eine andere Schwefel-Stickstoff-Verbindung der Zusammensetzung $(SN)_x$. Wird die Feuchtigkeit vollkommen ausgeschlossen, so entsteht die Verbindung $(SN)_x$ sogar als alleiniges Polymerisationsprodukt.

Aber auch ganz abgesehen von dieser Polymerisation ist S_2N_2 ein reaktionsfähiger Stoff. So entsteht z.B. beim Erwärmen einer Lösung von Dischwefel-dinitrid mit S_2Cl_2 sofort Thiotrithiazylchlorid, S_4N_3Cl. Von Wasser wird S_2N_2 zwar nicht benetzt und daher auch nicht rasch angegriffen; schüttelt man aber die Lösungen von S_2N_2 mit verdünnter Alkalilauge, so tritt sofort—schon in der Kälte—Hydrolyse ein:

$$4\,S_2N_2 + 4\,OH^- + 11\,H_2O \longrightarrow 2\,S_3O_6^{--} + S_2O_3^{2-} + 8\,NH_3 + 2\,H^+$$

C. POLYMERES SCHWEFELNITRID, S_nN_n

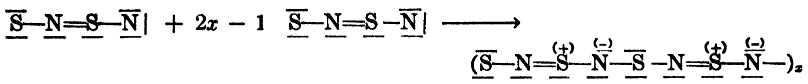
Überlässt man Dischwefel-dinitrid unter Ausschluss von Feuchtigkeit sich selbst, so findet, wenn man die Substanz unterhalb der Zersetzungstemperatur von S_2N_2 hält, eine langsame Polymerisation statt. Es entsteht eine feste Substanz, die schöne, faserige Kristalle bildet. Diese Kristalle haben einen fast metallischen, messingartigen Glanz. In dünner Schicht sieht die Substanz tiefblau aus. Dieser Stoff ist recht beständig. Erst oberhalb 130° tritt ein langsamer, von keiner Detonation begleiteter Zerfall in die Elemente ein.

Da die Substanz in keinem der gebräuchlichen Lösungsmittel löslich ist, konnte das Molekulargewicht bisher nicht bestimmt werden. Auch der Aufbau des Gitters konnte noch nicht festgelegt werden, da Einkristalle des Stoffes noch nicht erhalten worden sind. Einen Hinweis auf den Bau der Substanz geben nur einige andere physikalische Eigenschaften.

Es zeigte sich, dass S_nN_n diamagnetisch ist—wie das im übrigen auch für S_4N_4 gilt. Der Stoff hat also keine radikalische Natur. Das gepresste Pulver der Substanz erwies sich als ein Halbleiter für den elektrischen Strom. Die Leitfähigkeit nahm mit steigender Temperatur zu.

Die Bildung, die Faserstruktur und die physikalischen Eigenschaften von S_nN_n legen folgende Auffassung von der Struktur des Stoffes nahe:

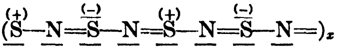
Die Polymerisation von S_2N_2 wird wohl, wie das bereits oben beschrieben wurde, zunächst zu Kettenpolymerisaten führen.



$$\underline{\overline{S}}-\underline{N}=\underline{S}-\underline{\overline{N}}| + 2x - 1\;\; \underline{\overline{S}}-\underline{N}=\underline{S}-\underline{\overline{N}}| \longrightarrow (\underline{\overline{S}}-\underline{N}=\underline{\overset{(+)}{S}}-\underline{\overset{(-)}{\overline{N}}}-\underline{\overline{S}}-\underline{N}=\underline{\overset{(+)}{S}}-\underline{\overset{(-)}{\overline{N}}}-)_x$$

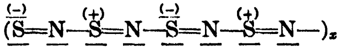
(XVa)

In diesem polymeren Stoff sollten nun die Elektronen weitgehend delokalisiert sein. Neben Formel (XVa) sollten also zahlreiche Grenzformeln zur Beschreibung der Resonanzfähigkeit des Moleküls notwendig sein, wie z.B. auch (XVb), (XVc), oder (XVd).



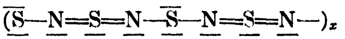
$$(\overset{(+)}{\underline{S}}-\underline{N}=\overset{(-)}{\underline{\overline{S}}}-\underline{N}=\overset{(+)}{\underline{S}}-\underline{N}=\overset{(-)}{\underline{\overline{S}}}-\underline{N}=)_x$$

(XVb)



$$(\overset{(-)}{\underline{S}}=\underline{N}-\overset{(+)}{\underline{S}}=\underline{N}-\overset{(-)}{\underline{S}}=\underline{N}-\overset{(+)}{\underline{S}}=\underline{N}-)_x$$

(XVc)



$$(\overline{\underline{S}}-\underline{N}=\underline{S}=\underline{N}-\overline{\underline{S}}-\underline{N}=\underline{S}=\underline{N}-)_x$$

(XVd)

D. TETRASCHWEFEL-DINITRID

Wenn man Tetraschwefel-tetranitrid in Schwefelkohlenstoff löst und diese Lösung mit Schwefel zusammen—zweckmässig im Autoklaven—auf Temperaturen zwischen 100 und 120° erhitzt, so kann man ein weiteres Schwefelnitrid erhalten.

Dieses Schwefelnitrid ist zuerst wohl von Muthmann und Clever (31) beobachtet worden. Diese Autoren haben ihm die Formel S_5N_2 zugeschrieben. Aber Meuwsen konnte nachweisen, dass dem durch Hochvakuumdestillation gereinigtem Produkt die Formel S_4N_2 zukommt (32). Der gleiche Stoff entsteht, wenn man S_4N_4 ohne Schwefelzusatz zusammen mit Schwefelkohlenstoff erhitzt (31), wenn man S_4N_4 zusammen mit Schwefel ohne Lösungsmittelzusatz auf 125° erhitzt (33), wenn man S_4N_4, CS_2 und Schwefel bei höherer Temperatur reagieren lässt und schliesslich auch in kleiner Ausbeute, wenn man S_4N_4 mit oder ohne Schwefelzusatz in Lösungsmitteln wie z.B. Benzol oder Toluol längere Zeit erhitzt (32). Der Bildungsmechanismus ist noch völlig ungeklärt. Markiert man die Reagentien mit radioaktivem Schwefel ^{35}S, so kann man erkennen, dass Schwefelkohlenstoff und Tetraschwefel-tetranitrid in der Weise miteinander reagieren, dass S_4N_2 und Polyrhodan, $(CNS)_x$, gebildet werden, wobei 30–35% des Schwefels von S_4N_2 vom CS_2 herrühren. Setzt man noch elementaren Schwefel zu, so werden zusätzlich Anteile dieses Schwefels in das S_4N_2 eingebaut, so dass dann bis zu 45% des Schwefels von S_4N_2 nicht aus dem eingesetzten S_4N_4 stammen. Der Polyrhodanschwefel rührt etwa zur Hälfte vom eingesetzten S_4N_4 und zur Hälfte vom CS_2 her. Setzt man S_4N_4 in benzolischer Lösung mit Schwefel um, so enthält das gebildete S_4N_2 nur etwa 5% Schwefel, der aus dem elementaren Schwefel stammt (33).

Danach ist es wohl ziemlich sicher, dass bei der Reaktion S_4N_4 in ein aktives Zwischenprodukt zerlegt wird, das vor allem mit CS_2 aber auch mit elementarem Schwefel weiterzureagieren vermag; aber die Natur dieses Zwischenstoffes ist unbekannt.

Ein weiteres Verfahren zur Herstellung von S_4N_2 (32) ist ebenfalls in seinem Verlauf noch ungeklärt aber recht überraschend. Es zeigte sich nämlich, dass man aus Tetraschwefeltetraimid (II) und Quecksilberacetat in pyridinischer Lösung eine feste, grüne Verbindung $Hg_5(NS)_8$ gewinnen kann (34). Schüttelt man diese Substanz in Schwefelkohlenstofflösung mit S_2Cl_2, so entsteht Hg_2Cl_2, $HgCl_2$ und S_4N_2.

S_4N_2 ist eine dunkelrote Substanz, die bei +23° schmilzt (35), aber sehr leicht unterkühlte Schmelzen bildet. Bei Temperaturen von +30° und bei tieferen Temperaturen ist die Verbindung diamagnetisch. Der Stoff ist schon bei Raumtemperatur nicht längere Zeit haltbar. Bei höherer Temperatur erfolgt der Zerfall, bei dem elementarer Schwefel entsteht, rascher, und bei 100° ist er explosionsartig. Auch die Zerfallsreaktion ist noch nicht geklärt.

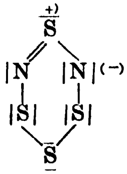
Wie die anderen Schwefelnitride löst sich S_4N_2 gut in organischen Lösungsmitteln. In Wasser ist es unlöslich; aber es erleidet langsam Hydrolyse, die durch Zusatz von Alkali beschleunigt wird und mit starker Alkalilauge im Sinne der Gleichung

$$4\,S_4N_2 + 18\,OH^- + 3\,H_2O \longrightarrow 7\,S_2O_3^{2-} + 2\,S^{2-} + 8\,NH_3$$

vor sich geht (32).

Für S_4N_2 sind verschiedene Formeln diskutiert worden. Mit den chemischen und physikalischen Eigenschaften scheint (XVI) sich gut vereinbaren zu lassen (35).

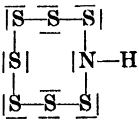
Diese Formel erscheint vor allem auch deshalb besonders erwägenswert, weil es sich gezeigt hat, dass es sechsgliedrige Ringsysteme gibt, die dem Gerüst von (XVI) weitgehend analog aufgebaut sind bis auf die Tatsache, dass ein S-Atom des Ringes durch Sauerstoff ersetzt ist.

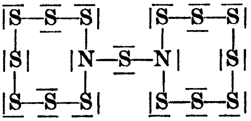


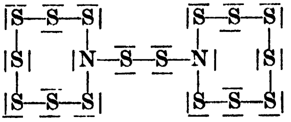
(XVI)

E. DIE SCHWEFELNITRIDE $S_{15}N_2$ UND $S_{16}N_2$

Eines der Produkte der Reaktion zwischen Schwefelchloriden und Ammoniak ist Heptaschwefelimid, S_7NH (36). Dieser Verbindung, die einen farblosen, gut kristallisierten Stoff darstellt, kommt die Formel (XVII) zu (37).


(XVII)


(XVIII)


(XIX)

Es zeigte sich nun, dass sich S_7NH mit SCl_2 bzw. mit S_2Cl_2 leicht umsetzen lässt (38). Bei dieser Reaktion werden die Schwefelnitride (XVIII) und (XIX) gebildet. Die Umsetzung geht glatt vor sich, wenn man Lösungen in Schwefelkohlenstoff verwendet und Pyridin zum Binden des gleichzeitig entstehenden Chlorwasserstoffs zusetzt.

Die beiden Schwefelnitride $S_{15}N_2$ und $S_{16}N_2$ sind gelbliche kristalline Substanzen, die in Schwefelkohlenstoff gut, in anderen organischen Lösungsmitteln fast gar nicht löslich sind. Wenn die Verbindungen durch mehrmaliges Umkristallisieren sorgfältig gereinigt sind, liegt der Schmelzpunkt von $S_{15}N_2$ bei 137° und der von $S_{16}N_2$ unscharf bei 95–100°.

Die beiden Schwefelnitride sind erstaunlich stabile Substanzen. $S_{15}N_2$ ist selbst bei 137° noch beständig und schmilzt ohne Zersetzung. Von Wasser werden die Stoffe nicht benetzt. Hydrolyse tritt nur bei längerem Erwärmen mit starker Alkalilauge ein.

Wenn man die Substanzen mit Piperidin reagieren lässt, so kann man Heptaschwefelimid, S_7NH, aus den Schwefelnitriden—besonders leicht aus $S_{16}N_2$—zurückerhalten. Diese Umsetzung ist gleichzeitig ein Beweis dafür, dass in den Verbindungen der S_7N-Rest mit seinem achtgliedrigen Ringsystem noch erhalten ist.

II. Thiodithiazyl- und Thiotrithiazyl-Verbindungen

A. THIODITHIAZYLCHLORID

Bereits im Jahre 1880 entdeckte Demarçay (39), dass sich S_4N_4 und S_2Cl_2 ziemlich rasch miteinander umsetzen können. Nimmt man die Reaktion in der Kälte vor, und arbeitet man entweder ohne Lösungsmittel oder mit Nitromethan als Lösungsmittel, so erhält man in quantitativer Ausbeute einen grünlichen kristallinen Stoff der Zusammensetzung S_3N_2Cl, Thiodithiazylchlorid:

$$S_4N_4 + S_2Cl_2 \longrightarrow 2\,S_3N_2Cl$$

Diese Bildungsreaktion, die sehr einfach aussieht, ist die Folge einer ganzen Reihe von Reaktionen. Man kann dies leicht erkennen, indem man den Schwefel des S_2Cl_2 durch radioaktiven Schwefel, ^{35}S, markiert. Dann zeigt sich, dass zwischen 40% und 60% des Schwefels von S_3N_2Cl aus dem im Überschuss verwendeten S_2Cl_2 stammen. Da einmal gebildetes S_3N_2Cl und S_2Cl_2 ihren Schwefel, wie ebenfalls gezeigt worden ist, nicht auszutauschen vermögen, lehrt dieser Befund, dass die Reaktion von S_4N_4 mit S_2Cl_2 über Zwischenstufen verläuft, die mit überschüssigem S_2Cl_2 Schwefel austauschen können. Man sieht ausserdem, dass es sich bei S_3N_2Cl nicht etwa um ein einfaches Addukt von S_4N_4 und S_2Cl_2 handeln kann. Ein derartiges Addukt, das man als S_4N_4,S_2Cl_2 formulieren könnte, müsste ja 33,3% Schwefel enthalten, der aus dem verwendeten S_2Cl_2 kommt (33).

Thiodithiazylchlorid entsteht auch in guter Ausbeute, wenn man auf S_4N_4 Nitrosylchlorid einwirken lässt (40):

$$S_4N_4 + 2\,NOCl \longrightarrow S_3N_2Cl + {}^1/_2\,S_2Cl_2 + 2\,N_2O$$

oder wenn man Trithiazylchlorid (IX) mit NO in Nitromethan als Lösungsmittel umsetzt:

$$8\,(ClSN)_3 + 24\,NO \longrightarrow 6\,S_3N_2Cl + 12\,NOCl + 3\,S_2Cl_2 + 12\,N_2O$$

Als Nebenprodukt schliesslich entsteht die Substanz auch, wenn man S_4N_4 und Thionylchlorid reagieren lässt.

Allen diesen Reaktionen ist gemeinsam, dass bei der Umsetzung zunächst das achtgliedrige oder sechsgliedrige Ringsystem der Ausgangssubstanz zerstört wird. Es bildet sich ein Bruchstück wie z.B. S_2N_2 oder auch SN, und diese Bruchstücke setzen sich mit S_2Cl_2 weiter um. Alle diese Reaktionen lassen sich also letzten Endes auf die von Demarçay entdeckte Bildungsreaktion zurückführen.

Dieser Gedankengang soll durch das folgende Reaktionsschema erläutert werden (40):

$$\begin{aligned} 8\,(ClSN)_3 + 24\,NO &\longrightarrow 24\,NOCl + 12\,S_2N_2 \\ 12\,S_2N_2 + 12\,NOCl &\longrightarrow 6\,S_2Cl_2 + 6\,S_2N_2 + 12\,N_2O \\ 6\,S_2N_2 + 3\,S_2Cl_2 &\longrightarrow 6\,S_3N_2Cl \end{aligned}$$

Wie die Umsetzungen im Einzelnen vor sich gehen, kann natürlich nicht gesagt werden.

Thiodithiazylchlorid ist eine feste, gut kristallisierte Substanz, die dunkelgrün aussieht und fast metallisch schimmert. Sie ist in organischen Lösungsmitteln unlöslich und wird von Wasser rasch hydrolysiert. Das Molekulargewicht ist nicht bekannt. Vermutlich handelt es sich bei S_3N_2Cl um einen polymeren Stoff, dessen Molekulargewicht ein Vielfaches des Formelgewichtes beträgt. Das Gleiche gilt von dem Bromid S_3N_2Br (40).

Von Versuchen, die Natur des Thiodithiazylchlorids durch chemische Umsetzungen zu klären, ist vielleicht das Ergebnis der Umsetzung mit SO_3 bemerkenswert. Es zeigte sich nämlich (40), dass bei der Einwirkung von Schwefeltrioxyd ein rotbraunes, sehr hygroskopisches Addukt $S_3N_2Cl \cdot 2\,SO_3$ entsteht, das bei der Hydrolyse u.a. Amidosulfonsäure bildet, in dem also das SO_3 sicher am Stickstoff gebunden ist. Bemerkenswert ist weiter, dass aus Thiodithiazylchlorid sehr leicht Thiotrithiazylchlorid entsteht, wenn man es einige Zeit unter einem indifferenten organischen Lösungsmittel—z.B. Tetrachlorkohlenstoff—erhitzt:

$$6\,S_3N_2Cl \longrightarrow 4\,S_4N_3Cl + S_2Cl_2$$

B. THIOTRITHIAZYLCHLORID

Beständiger als Thiodithiazylchlorid ist die ebenfalls von Demarçay (39) entdeckte Verbindung Thiotrithiazylchlorid, S_4N_3Cl. Wie bereits oben beschrieben, bildet sich diese Substanz aus Thiodithiazylchlorid beim Erwärmen. Man kann sie aber auch direkt aus S_4N_4 und S_2Cl_2 erhalten:

$$2\,S_2Cl_2 + 3\,S_4N_4 \longrightarrow 4\,S_4N_3Cl$$

wenn man in der Hitze und zweckmässig mit einem indifferenten Lösungsmittel arbeitet (41). Durch Markieren mit radioaktiven Isotopen kann man wieder feststellen, dass auch bei dieser Umsetzung wechselnde Mengen Schwefel, die aus dem Dischwefeldichlorid stammen, in das Reaktionsprodukt S_4N_3Cl eingebaut werden. Diese Schwefelmenge ist von dem angewandten Konzentrationsverhältnis abhängig. Da S_4N_3Cl beim Erhitzen mit S_2Cl_2 seinen Schwefel nicht austauscht, zeigt dieses Ergebnis, dass die Umsetzung über Zwischenstufen verlaufen muss, die zu einem derartigen Austausch befähigt sind.

Andere Bildungsreaktionen für Thiotrithiazylchlorid sind die Umsetzung von S_4N_4 mit Chlorwasserstoff (27), bei der ein Addukt $S_4N_4 \cdot 4\ HCl$ entsteht, das bei Anwesenheit von Feuchtigkeitsspuren in S_4N_3Cl, Ammoniumchlorid und Chlor verwandelt wird, die Reaktion von Trithiazylchlorid mit Dischwefeldichlorid (42) und die Umsetzung von S_4N_4 mit Thionylchlorid in der Hitze (42). Keine dieser Reaktionen ist in ihrem Mechanismus bisher aufgeklärt worden.

Thiotrithiazylchlorid ist eine hellgelbe, feste Substanz, die, wenn man Feuchtigkeit ausschliesst, recht beständig ist. Erhitzt man die Substanz im Vakuum auf etwa 170°, so wird S_4N_3Cl gespalten, und es kann aus den Reaktionsprodukten S_4N_4 heraussublimiert werden. Erhitzt man den Stoff an der Luft, so tritt natürlich eine rasche Verbrennung ein.

S_4N_3Cl hydrolysiert mit Wasser unter Bildung eines schwarzen Bodenkörpers, in dem ein Hydroxyd der Zusammensetzung S_3N_2OH nachgewiesen worden ist (43).

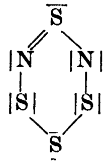
Die bemerkenswerteste chemische Reaktion des Thiotrithiazylchlorides stellt die Umsetzung mit konzentrierten Sauerstoffsäuren oder mit konzentrierten Bromwasserstoff- bzw. Rhodanwasserstoff-Lösungen dar. Bei diesen Reaktionen entstehen andere Thiotrithiazylverbindungen, z.B., $(S_4N_3)NO_3$ (44), $(S_4N_3)HSO_4$ (43), (S_4N_3)-SCN (43), und $(S_4N_3)Br$. Diese Umsetzungen weisen darauf hin, dass unter geeigneten Bedingungen wohl mit der Existenz des Ions $[S_4N_3]^+$ gerechnet werden muss.

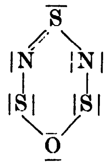
Die Konstitution der Thiotrithiazylverbindungen ist, obgleich sie Gegenstand zahlreicher Untersuchungen gewesen ist, noch nicht geklärt (45). Es ist nicht einmal sicher, ob den Stoffen das einfache Formelgewicht zukommt. Es wird interessant sein zu klären, aus welchem Grund sich gerade diese Thiotrithiazylverbindungen so leicht aus den verschiedenen Schwefel-Stickstoff-Verbindungen bilden und warum sie so verhältnismässig stabil sind.

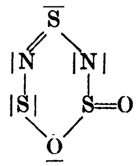
III. Verbindungen, die Ringsysteme enthalten, die aus Schwefel, Stickstoff und Sauerstoff aufgebaut sind

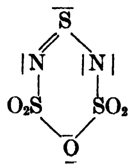
Viele der bisher beschriebenen Schwefel-Stickstoff-Verbindungen hatten ein Grundgerüst, das man als gewellte acht-oder sechsgliedrige Ringsysteme auffassen kann. Denkt man sich in der vorgeschlagenen

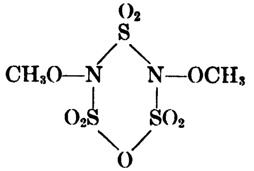
Formel für S_4N_2 (XVI), die ein sechsgliedriges Ringsystem darstellt, den Schwefel durch den Sauerstoff ersetzt, so kommt man zu Formel (XX). Tatsächlich ist eine Verbindung mit der Formel S_3N_2O, wie sie der hypothetischen Struktur (XX) entsprechen würde, beschrieben worden. Aber es ist noch ungewiss, ob diese Substanz tatsächlich ein derartiges sechsgliedriges Ringsystem enthält. Dagegen konnte $S_3N_2O_2$ als stabile Verbindung erhalten werden, und für diesen Stoff ist ein Ringsystem (XXI) sehr wahrscheinlich gemacht worden, und ebenso scheint für $S_3N_2O_5$ Formel (XXII) gesichert. Schliesslich konnte die Existenz dieser Gruppe von sechsgliedrigen Ringsystemen durch die Synthese von (XXIII) mit Stickstoff höherer Oxydationszahl noch gesichert werden. Diese kleine Gruppe von Verbindungen enthält vorwiegend thermisch stabile Stoffe, die allerdings mit Wasser infolge der leichten Angreifbarkeit der Schwefel-Sauerstoff-Bindung leicht Hydrolyse erleiden.


(XVI)


(XX)

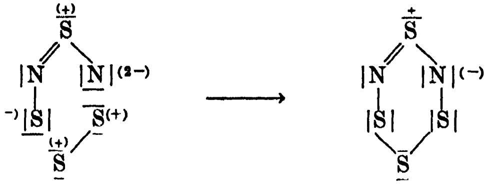

(XXI)


(XXII)


(XXIII)

A. TRISCHWEFEL-DISTICKSTOFF-MONOXYD

Eine Substanz der Zusammensetzung S_3N_2O ist aus dem schon früher erwähnten $Hg_5(NS)_8$ gewonnen worden (46). Während sich $Hg_5(NS)_8$ mit S_2Cl_2 zu Tetraschwefeldinitrid umsetzt (34), reagiert dieselbe Substanz mit Thionylchlorid zu S_3N_2O, $HgCl_2$ und Hg_2Cl_2. Möglicherweise kann man diese Reaktion so verstehen, dass in $Hg_5(NS)_8$ am Quecksilber gebunden $[S_2N_2]^{2-}$ vorliegt. An diese Gruppe könnte sich S_2^{2+} aus S_2Cl_2 anlagern und so (XVI) aufbauen:



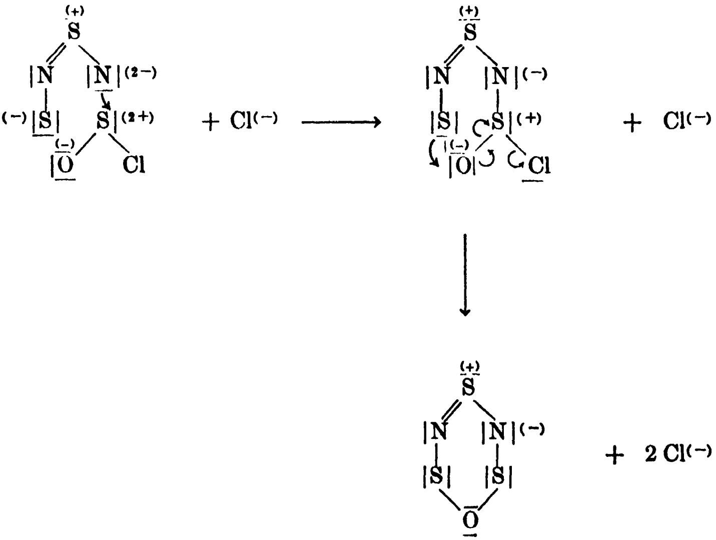
(XVI)

Durch die vorgeschlagene Formulierung soll allerdings nicht zum Ausdruck gebracht werden, dass die Umsetzung in einem Schritt stattfindet. Es ist vielmehr anzunehmen, dass S_2Cl_2 zunächst im Sinne von:

$$S_2Cl_2 \rightleftharpoons S_2Cl^+ + Cl^-$$

dissoziiert, und dass dieses Kation mit $[S_2N_2]^{2-}$ reagiert. Erst in einem zweiten Schritt sollte dann das Chlor als Cl^- abgespalten und der Ring geschlossen werden.

In ganz analoger Weise sollte sich $OSCl_2$ mit dem anionischen Bestandteil von $Hg_5(NS)_8$ umsetzen und dann (XX) aufbauen:



S_3N_2O ist eine schon bei Zimmertemperatur wenig beständige rote Flüssigkeit. Bei 0° kann man sie einige Stunden unzersetzt aufbewahren. Bei der thermischen Zersetzung entsteht neben anderen Stoffen S_4N_4.

B. TRISCHWEFEL-DISTICKSTOFF-DIOXYD

Während bei der Umsetzung von Tetraschwefel-tetranitrid mit Thionylchlorid in der Hitze verhältnismässig glatt Thiotrithiazylchlorid gebildet wird, verläuft diese Reaktion in der Kälte anders und unter Bildung einer Reihe von Schwefelverbindungen. Lässt man die beiden Stoffe in Nitromethan bei 20° miteinander reagieren, so entsteht Thiodithiazylchlorid, S_3N_2Cl, daneben S_4N_2, S_2Cl_2 oder S_3Cl_2 und die Sauerstoff enthaltende Verbindung $S_3N_2O_2$. Trischwefel-distickstoff-dioxyd wird hierbei etwa mit einer Ausbeute von 25% (bezogen auf den Stickstoff) gefunden. Will man die Ausbeute an diesem Stoff erhöhen, so muss man S_4N_4 mit siedendem Thionylchlorid umsetzen und zweckmässig einen Strom von Schwefeldioxyd durch das Reaktionsgemisch durchblasen (47). Die Umsetzung kann durch die Gleichung

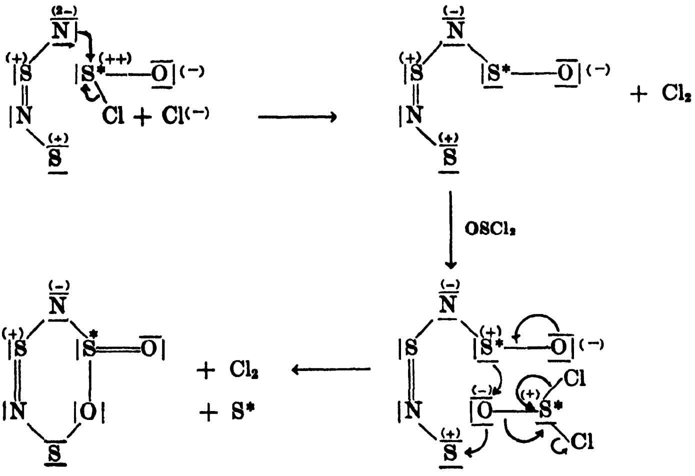
$$S_4N_4 + 2\,OSCl_2 \longrightarrow S_3N_2O_2 + S_2N_2 + 2\,Cl_2 + S$$

beschrieben werden. S_2N_2 reagiert mit dem Schwefel weiter zu S_4N_2. Durch welche Reaktion die Bildung von Thiodithiazylchlorid —und in der Hitze von Thiotrithiazylchlorid—verursacht wird, ist allerdings noch nicht klar.

Markiert man den Thionylchlorid-Schwefel durch das radioaktive Isotope ^{35}S, so kann man erkennen, dass eines der Schwefelatome des $S_3N_2O_2$ aus dem Thionylchlorid stammen muss, während die restlichen zwei Schwefelatome aus dem Schwefelnitrid gekommen sein müssen. Man hat sich danach die Umsetzung etwa folgendermassen vorzustellen:

Zunächst wird S_4N_4 in zwei S_2N_2-Gruppen aufgespalten. Dieses S_2N_2 setzt sich mit Thionylchlorid um, das wohl zunächst dissoziiert oder doch im Sinne der folgenden Gleichung polarisiert wird:

$$OSCl_2 \rightleftharpoons OSCl^+ + Cl^{(-)}$$



(XXI)

Es sollte dann zuerst ein Addukt und dann daraus ein Zwischenprodukt entstehen, das mit überschüssigem $OSCl_2$ zu $S_3N_2O_2$, Schwefel und Chlor reagiert.

Der Schwefel der Oxydationszahl +4, der in der Verbindung (XXI) gebunden an zwei Sauerstoffatome enthalten ist, kann aus dem Stoff als Schwefeldioxyd abgespalten werden. Schon wenn man $S_3N_2O_2$ mit einem Strom feuchten Stickstoffs bei Raumtemperatur behandelt, findet die Umsetzung statt:

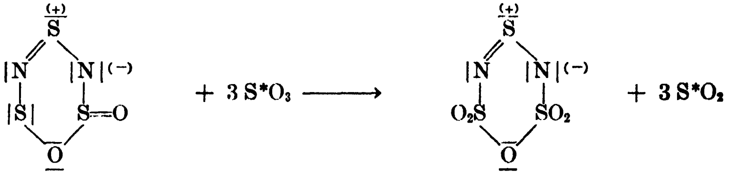
$$2\,S_2N_2S^*O_2 \longrightarrow S_4N_4 + 2\,S^*O_2$$

Die Tatsache, dass der Schwefel des gebildeten Schwefeldioxyds aus dem ursprünglich eingesetzten Thionylchlorid stammt, zeigt deutlich, dass ein Wertigkeitsausgleich durch Resonanz bei den Schwefelatomen, die das $S_3N_2O_2$-Molekül aufbauen, nicht möglich ist (48).

$S_3N_2O_2$ ist gut kristallisiert und sieht schwach gelblich aus. Es schmilzt bei 100, 7° unzersetzt, zersetzt sich aber bei weiterem Erhitzen. Viele organische Lösungsmittel wie z.B. Benzol oder Alkohole lösen die Verbindung, und das Molekulargewicht kann kryoskopisch bestimmt werden. Von Wasser wird die Substanz nicht benetzt. Aber an der feuchten Luft oder mit feuchtem Stickstoff zusammengebracht tritt der oben beschriebene Zerfall in S_4N_4 und SO_2 ein. Natronlauge hydrolysiert rasch im Sinne der Gleichung

$$S_3N_2O_2 + 4\,H_2O \longrightarrow (NH_4)_2S_3O_6$$

Für eine Konstitution des $S_3N_2O_2$ im Sinne der Formel (XXI) spricht ferner eine Oxydationsreaktion, die zu $S_3N_2O_5$ (XXIIa) führt (49). Diese Oxydation verläuft sehr glatt, wenn man auf festes Trischwefel-distickstoff-dioxyd Schwefeltrioxyd aufkondensiert. Aus dem Reaktionsgemisch kann man dann Trischwefeldistickstoffpentoxyd heraussublimieren. Wenn man das SO_2 mit ^{35}S markiert, dann kann man erkennen, dass die Umsetzung im Sinne der Gleichung verläuft:


(XXI) (XXIIa)

Diese Reaktion zeigt wieder, wie das bereits früher (vgl. S. 214) erwähnt worden ist, dass Schwefeltrioxyd ein gutes Oxydationsmittel für Schwefel der Oxydationszahl +4 und der Koordinationszahl 3 darstellt, und es erscheint bemerkenswert, dass der Schwefel der Oxydationszahl +4 und der Koordinationszahl 2, der an die beiden Stickstoffatome gebunden ist, nicht oxydiert wird. Man kann in diesem Zusammenhang vielleicht daran erinnern, dass SO_2 und SO_3 ihren Schwefel nicht auszutauschen vermögen (50), und das bedeutet ja, dass SO_2, in dem ebenfalls Schwefel der Oxydationszahl +4 und der Koordinationszahl 2 vorliegt, durch SO_3 nicht oxydiert wird. Dieses Ergebnis steht also mit der Beobachtung, die man bei der Oxydation von $S_3N_2O_2$ macht, in bestem Einklang.

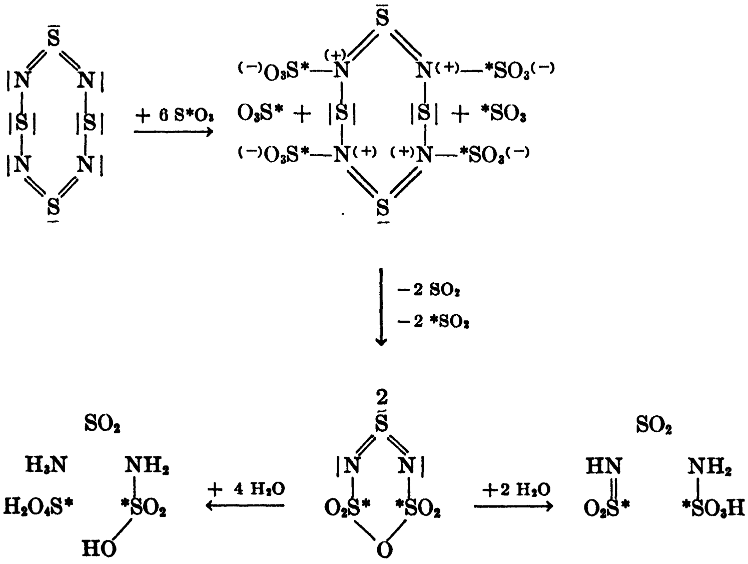
C. TRISCHWEFEL-DISTICKSTOFF-PENTOXYD

Eine Substanz der Zusammensetzung $S_3N_2O_5$ erhält man nicht nur, wenn man Trischwefel-distickstoff-dioxyd mit Schwefeltrioxyd umsetzt, sondern auch, wenn man Tetraschwefel-tetranitrid mit SO_3 reagieren lässt.

S_4N_4 lagert leicht Schwefeltrioxyd unter Bildung eines ziegelroten Adduktes (XXIV) an (51). Beim Erwärmen mit überschüssigem

SO_3 entsteht aus diesem Addukt Schwefeldioxyd und $S_3N_2O_5$. Markiert man wieder das Schwefeltrioxyd mit dem Schwefelisotopen ^{35}S, so kann man erkennen, dass der Schwefeltrioxyd-Schwefel diesmal in das entstehende Molekül eingebaut wird. Nur eines der Schwefelatome von $S_3N_2O_5$ stammt aus dem angewandten S_4N_4. Dieser Befund legt den im Folgenden angedeuteten Reaktionsmechanismus nahe. Das entstandene Produkt (XXII) ist dann als ein Derivat—und zwar ein substituiertes Amid der Dischwefelsäure $H_2S_2O_7$—aufzufassen.

Für die Konstitution ist besonders die Hydrolyse beweisend, bei der pro Mol immer ein Mol Schwefeldioxyd entsteht. Dieses Schwefeldioxyd enthält, wenn man eine Markierung der Schwefelatome vornimmt, wie es in dem Schema angedeutet wird, niemals radioaktiven Schwefel. Neben dem Schwefeldioxyd entsteht bei der Hydrolyse Amidosulfonsäure, Sulfimid—bzw. als dessen Folgeprodukt Sulfamid—, Schwefelsäure und Ammoniak. Immer gehen $^2/_3$ des vorhandenen Schwefels in Verbindungen mit Schwefel der Oxydationszahl +6 über, während $^1/_3$ des Schwefels die Verbindung mit Schwefel der Oxydationszahl +4, SO_2, bildet (49).



(XXIIb)

Trischwefel-distickstoff-pentoxyd ist eine farblose, stark lichtbrechende, schön kristallisierte Substanz, die sich ohne Zersetzung in organischen Lösungsmitteln wie z.B. Nitrobenzol, Benzol und Benzolhomologen löst. Das Molekulargewicht kann kryoskopisch bestimmt werden. Der Stoff ist leicht sublimierbar. Schon durch Spuren von Wasser wird die Substanz im oben angedeuteten Sinne hydrolysiert.

D. *N,N'*-DIMETHOXY-CYCLO-SULFAMIDO-DISULFONSÄURE-ANHYDRID

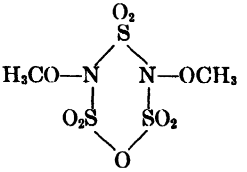
Es gelang, noch eine weitere Substanz herzustellen, in der ein sechsgliedriges Ringsystem mit drei Schwefel-, zwei Stickstoff- und einem Sauerstoff-Atom im Ring enthalten sind. Dazu wurde zunächst Sulfurylchlorid mit *O*-Methylhydroxylamin umgesetzt, und das feste und farblose Dimethoxysulfamid (XXV) erhalten (52):

$$O_2SCl_2 + 4\,H_2NOCH_3 \longrightarrow \underset{\text{(XXV)}}{O_2S(NH{-}OCH_3)_2} + 2\,[H_3NOCH_3]Cl$$

Mit Schwefeltrioxyd setzt sich dieses Produkt leicht um. Es entsteht Wasser, bzw. bei Verwendung von überschüssigem SO_3 Polyschwefelsäure und die Verbindung (XXIII), die letzten Endes wieder ein Derivat der Dischwefelsäure darstellt.

Der Stoff sieht farblos aus, ist gut kristallisiert und schmilzt bei 91° unter Zersetzung. Die Verbindung löst sich in organischen Lösungsmitteln wie Benzol und wird durch Wasser nicht benetzt. Wie alle Verbindungen mit diesem sechsgliedrigen Ringsystem kann man den Stoff im Vakuum leicht sublimieren (52).

Als Derivat der Dischwefelsäure kann man (XXIII) natürlich leicht hydrolysieren, wenn man die Lösung in einem organischen Lösungsmittel mit Wasser schüttelt. Durch Erhitzen mit Äthern lässt sich in (XXIII)—wie übrigens auch in der Verbindung XXII—

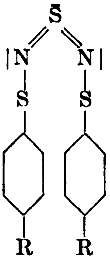


(XXIII)

die S–O–S-Brücke öffnen und es entstehen Ester der Dimethoxysulfamido-disulfonsäure.

IV. Thiodithiazyl-diaryle

Tetraschwefel-tetranitrid sezt sich schon in der Kälte mit Arylmagnesiumbromid-Lösungen um. Nach der Zersetzung des entstandenen Reaktionsproduktes mit Wasser kann man aus dem Reaktionsgemisch Thiodithiazyl-diaryle isolieren. Den Verbindungen kommt die Formel (XXIV) zu. Bisher sind Stoffe mit R = H, R = OCH_3 und R = Cl isoliert worden. Bei diesen Substanzen handelt es sich um kristallisierte orangegelbe bis braungelbe Stoffe, die in organischen Lösungsmitteln löslich und in Wasser unlöslich sind. Die Verbindungen sind sehr beständig; sie schmelzen unzersetzt. Der Grundkörper (R = H) schmilzt z.B. bei 105°.



(XXIV)

Für die Konstitution ist beweisend, dass bei der Reduktion des Grundkörpers Thiophenol entsteht (53).

Mit Alkylmagnesiumhalogenid entstehen keine analogen stabilen Reaktionsprodukte. Meuwsen (24) hat mit Äthylmagnesiumbromid das blutrote flüssige, wenig beständige $C_2H_6S_2N_2$ erhalten.

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Metal–Ammonia Solutions

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I. Introduction

The dissolution of a metal in liquid ammonia is one of the most fascinating phenomena in chemistry. Since Weyl's (169) first study of metal–ammonia solutions in 1864, more than a thousand articles have appeared in the literature on this subject. It is significant that there appears to be no decline in the rate of such publication (even excluding work where the primary interest lies in the reducing properties of the solutions). No general agreement has been reached as to the nature of the solutions. Several excellent reviews have appeared in recent years (8,97,174). It is the purpose of this article to describe those properties of metal–ammonia solutions which are significant to the formulation of detailed models of the solutions.

It will be noted that, in discussions of the various experimental data, references are made to certain models of metal–ammonia solutions. In recent years, a variety of models have been proposed, each of which applies to a rather restricted concentration range. There are at least three concentration ranges for which separate models must be formulated: (*1*) the "extremely dilute" region (comprising solutions less concentrated than about $0.005M$), (*2*) the "moderately concentrated" region (concentrations between about 0.005 and $1M$), and (*3*) the "extremely concentrated" or "metallic" region (concentrations greater than $1M$). Of course, there are no sharp divisions between these regions, but it is remarkable that many phenomena are characteristic of only one of these concentration regions.

All metal–ammonia solutions are metastable. If they are allowed to stand for long periods, or if suitable catalysts are present (16), decomposition to hydrogen and the metal amide occurs (5,6,116):

$$M + x\,NH_3 = {}^{x}/_{2}\,H_2 + M(NH_2)_x \qquad (1)$$

But if pure reagents and clean apparatus are used, and if the solutions are kept cold, decomposition may be held to 0.1% per day (34). Except for amide formation, a metal may be recovered from its solution by vaporizing the ammonia. Thus, *in principle*, the dissolution of a metal in ammonia is a reversible process. In this respect, metal–ammonia solutions are similar to solutions of metals in methylamine (91), ethylamine (91), ethylenediamine (91), propylenediamine (45), tetrahydrofuran (36,170), diethylene glycol dimethyl ether (36,170), ethylene glycol dimethyl ether (36,170), the cyclic tetramer of propylene oxide (36,170), water (84,173), methanol (84), and ethanol (84). On the other hand, metal–ammonia solutions are different from alkali metal–pyridine "solutions," where salt-like compounds are formed (38–40).

II. Solubilities

A. METALS SOLUBLE IN AMMONIA

To find the metals which dissolve in liquid ammonia, one need simply look at the top of a table of aqueous oxidation potentials. The only metals in Table I which have not been observed to dissolve in

TABLE I
Aqueous Oxidation Potentials (111)

Couple	$E°$
$Eu = Eu^{2+} + 2e^-$	3.40
$Yb = Yb^{2+} + 2e^-$	3.11
$Sm = Sm^{2+} + 2e^-$	ca. 3.1
$Li = Li^+ + e^-$	3.04
$Am = Am^{2+} + 2e^-$	ca. 3.0 (146)
$K = K^+ + e^-$	2.92
$Rb = Rb^+ + e^-$	2.92
$Cs = Cs^+ + e^-$	2.92
$Ra = Ra^{2+} + 2e^-$	2.92
$Ba = Ba^{2+} + 2e^-$	2.90
$Sr = Sr^{2+} + 2e^-$	2.89
$Ca = Ca^{2+} + 2e^-$	2.87
$Na = Na^+ + e^-$	2.71
$Ac = Ac^{3+} + 3e^-$	ca. 2.6
$R^a = R^{3+} + 3e^-$	2.52–2.25
$Mg = Mg^{2+} + 2e^-$	2.37

[a] Rare earths.

ammonia are samarium, americium, radium, actinium, and the rare earths which do not exhibit the +2 oxidation state. It is very likely that the first three of these metals will be found to be soluble, but there is considerable doubt regarding actinium and the rare earths which do not exhibit the +2 oxidation state. After all, these latter metals are at the bottom of the table with magnesium, which is very difficultly soluble in ammonia (22).

It appears that the factors which cause a metal to have a high oxidation potential (high solvation energy, low ionization potential, low sublimation energy) are the same as those which cause it to have a high solubility in ammonia. This observation is consistent with the concept that dilute metal–ammonia solutions are electrolytic; that is, they contain ammoniated metal ions and electrons.

It is possible to prepare relatively unstable ammonia solutions of metals less electropositive than those in Table I by cathodic reduction of the appropriate metal salt solutions. For example, solutions of aluminum and aluminum iodide (124) and of beryllium and beryllium chloride (81) have been prepared in this manner. Even more fascinating are the blue solutions of tetraalkylammoniums which are prepared by cathodic reduction of tetraalkylammonium halide solutions (44,155,156). Recent work indicates that these solutions are similar to alkali metal solutions (56,77,109).

B. LIQUID-LIQUID PHASE SEPARATION

A striking feature of most metal–ammonia systems is the existence of liquid-liquid miscibility gaps. That is, it is possible to have two immiscible solutions of the same metal at equilibrium. The heavier phase is blue and less concentrated in metal than the less dense, bronze-colored phase. This type of behavior has been observed for lithium (60,100), sodium (104,154), potassium (11), calcium (92), strontium (127), and barium (4,127), but cesium apparently shows no miscibility gap (58).

For example, consider the process of gradually adding ammonia to a saturated (10.8 molal) solution of sodium in ammonia at −47.5°C. At first the solution is simply diluted, but when a concentration of 3.95 molal is reached, a second liquid phase of concentration 1.51 molal separates. Continued addition of ammonia causes the second phase to grow at the expense of the first phase until only the second phase remains. Further addition of ammonia simply dilutes the

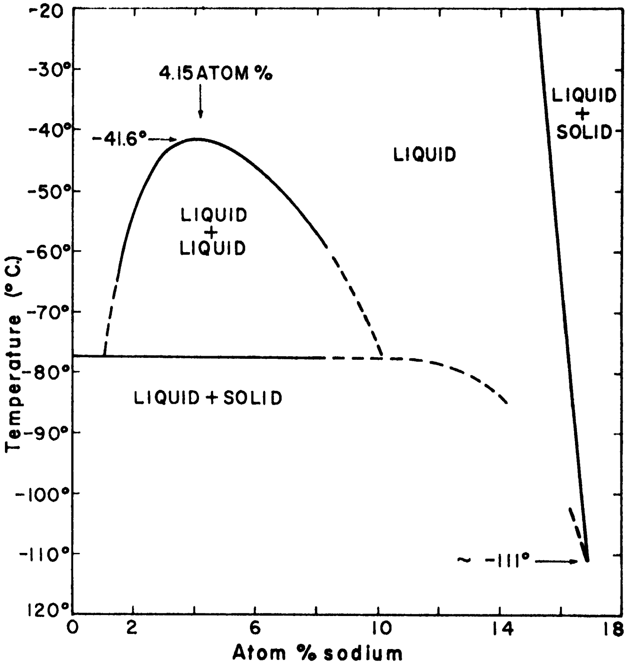


Fig. 1. Sodium–ammonia phase diagram (data from ref. 104 and Table III).

remaining solution. The phase diagram for sodium and ammonia is given in Figure 1. The phase diagram for other metal–ammonia systems are known very incompletely, but the eutectic temperatures and compositions given in Table II have been reported.

TABLE II
Metal–Ammonia Eutectics (10,11)

Metal	Temp., °C.	Mole % metal (approx.)
Li	−185	22
K	−157	15
Cs	−118	—
Ca	−87	12
Sr	−89	7
Ba	−89	7.7

Pitzer (147) has proposed that the separation of metal–ammonia solutions into two liquid phases is a liquid-vapor phase separation of the metal within the ammonia dielectric. The concentrated phase thus corresponds to the liquid metal, and the dilute phase corresponds to the vaporized metal. The effect of the dielectric is to make metal–ammonia solutions behave as metals with reduced energy and increased distance properties. Thus the "vapor-liquid" equilibrium is just one of several expected phenomena.

C. SOLUBILITIES OF ALKALI METALS

Solubilities of the alkali metals at various temperatures are given in Table III.

TABLE III

Temp., °C.	G. atom metal/1000 g. NH_3	Moles NH_3/ g. atom metal
	Lithium (76,101)	
0	16.31	3.60
−33.2	15.66	3.75
−39.4	16.25	3.61
−63.5	15.41	3.81
	Sodium (73,102,153)	
22	9.56	6.14
0	10.00	5.87
−30	10.63	5.52
−33.8	10.72	5.48
−33.5	10.93	5.37
−50	10.89	5.39
−70	11.29	5.20
−105	11.79	4.98
	Potassium (73,74,102,153)	
0	12.4	4.68, 4.74
−33.2	11.86	4.95
−50	12.3	5.05, 4.79
−100	12.2	4.82
−33.5	12.05	4.87
	Cesium (58)	
−50	25.1	2.34

D. ALKALINE EARTH HEXAMMONIATES

Calcium, strontium, barium, and probably europium and ytterbium cannot exist in equilibrium with their ammonia solutions. These metals form solid ammoniates which are good electrical conductors and have metallic appearance. Early workers (7,92,129,151) found these compounds to be hexammoniates, but some recent work casts doubt on these findings and suggests that nonstoichiometric amounts of ammonia are combined with the metals (127).

Biltz and Huttig give the following equations to represent the equilibrium pressure over the metal–metal ammoniate systems (7):

$Ca(NH_3)_6$:

$$\log P_{\text{atm}} = -2258/T + 1.75 \log T - 0.0030T + 3.3 \qquad (2)$$

$Sr(NH_3)_6$:

$$\log P_{\text{atm}} = -2168/T + 1.75 \log T - 0.0034T + 3.3 \qquad (3)$$

$Ba(NH_3)_6$:

$$\log P_{\text{atm}} = -2112/T + 1.75 \log T - 0.0034T + 3.3 \qquad (4)$$

Some idea of the uncertainity in these data may be gained from the fact that these investigators report a 0°C. equilibrium pressure of 23 mm. for $Ca(NH_3)_6$, whereas Marshall and Hunt (127) report a corresponding pressure of 46 mm.

Consider the process of evaporating ammonia from a dilute solution of calcium in liquid ammonia at -32.5°C. (92). When the concentration of calcium reaches a value somewhat less than $0.1M$, a bronze-colored solution forms as a second phase. The pressure remains constant at approximately one atmosphere during further removal of ammonia until only the bronze-colored solution remains. This solution may then be concentrated to the point where the solid hexammoniate separates and the pressure is 47.18 cm. When sufficient ammonia is evaporated so that only the hexammoniate remains, further ammonia removal yields metallic calcium, and an equilibrium pressure of 0.18 cm. is established. Theoretically, all the ammonia could be removed until only metallic calcium were left, but, in practice, a large fraction of the ammoniate decomposes to calcium amide and hydrogen.

Pure magnesium hexammoniate has never been prepared, but some work by Loomis indicates that solid solutions of $Mg(NH_3)_6$ in mercury may be prepared (121).

The europium and ytterbium systems have not been studied quantitatively (164).

III. Vapor Pressures

Kraus (93) determined the pressure differences between pure ammonia and various sodium solutions ranging in concentration from about 0.1 to 1.0*M*. When the apparent molecular weights of the sodium (calculated according to Raoult's law) are plotted

TABLE IV
References to Vapor Pressure Studies

Temp., °C.	NH_3/metal range covered	Ref.
	Lithium	
−63.8	satd. to 57	127
−45.3	satd. to 685	127
−39.4	satd. to 60	101
	Sodium	
−63.8	satd. to 74	127
−45.3	satd. to 694	127
−33	satd. to 11	99
∼15	36 to 470	93
	Potassium	
−50.4	satd. to 12	74
−33.5	satd. to 21	74
0.0	satd. to 10	74
	Cesium	
−50	satd. to 17	58
	Calcium	
−63.8	satd. to 28	127
−45.3	satd. to 19	127
	Strontium	
−63.8	satd. to 53	127
	Barium	
−63.8	satd. to 40	127
−45.3	satd. to 23	127

against the logarithm of the dilution, a straight line is obtained. The molecular weight for 0.1*M* sodium is 22.8, and that for 1*M* sodium is 31.3. There is considerable doubt whether Raoult's law is applicable to these relatively concentrated solutions, but the data suggest that, in the neighborhood of 0.1*M*, the solute exists in the form of monatomic units (such as sodium ion–electron ion pairs), and that in more concentrated solutions considerable polymerization occurs.

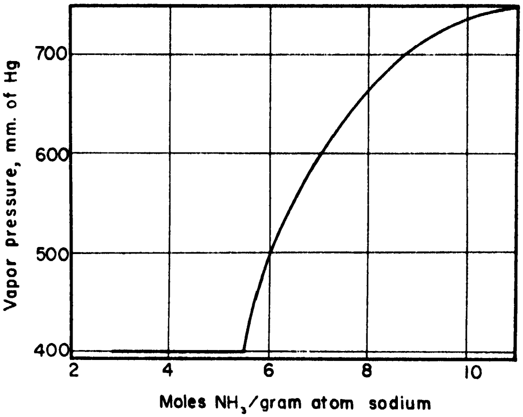


Fig. 2. Vapor pressure of ammonia over sodium–ammonia solutions at −33.8 (174; reproduced by permission; data from ref. 99).

Marshall and Hunt (127) have calculated relative activity coefficients for the alkali metals from their own and literature vapor pressure data, and it is apparent that there are large differences among the metals. From the form of the activity coefficient–concentration curve for sodium, it seems that the calculations of Kraus have very little meaning. Unfortunately, no vapor pressure studies have been carried out at sufficiently high dilution to permit the calculation of absolute activity coefficients. Such data would be extremely valuable, because with them it would be possible to calculate the free energies of dissolved metals.

In Table IV, literature references to various vapor pressure studies are given. In Figure 2, the vapor pressure of ammonia over concentrated sodium solutions is plotted against the NH_3/Na ratio.

IV. Densities

A. DENSITIES OF METAL SOLUTIONS

The dissolution of a metal in ammonia is accompanied by a large net increase in volume. Densities of the solutions have been determined for lithium (70,75), sodium (63,73,75,87,99,135,160), potassium (73,75), and cesium (58). Selected values of the densities and calculated volume increments are tabulated in Tables V and VI. It is remarkable that a saturated solution of lithium at room temperature possesses a density lower than that of any other known liquid at room temperature. The volume increments for sodium and potassium pass through a maximum at about 3*M*, but the volume increments for lithium and cesium steadily increase and decrease, respectively, as the solutions become more dilute.

TABLE V

Densities as a Function of Concentration

Lithium (75,125) −33.2°			Sodium (73) −33.8°		
Mole fraction of lithium	Density	ΔV, cc./g. atom of metal	NH_3/Na	Density	ΔV, cc./g. atom of metal
.0331	.639	46.7	5.48	.5781	41.01
.0571	.611	46.1	37.84	.6603	43.03
.1180	.554	42.5	48.04	.6653	41.95
.1616	.518	41.4	55.17	.6681	40.45
.2105	.490	37.9	64.14	.6704	39.51

Potassium (73) −33.2°			Cesium (58) −50°		
NH_3/K	Density	ΔV, cc./g. atom of metal	NH_3/Cs	Density	ΔV, cc./g. atom of metal
4.95	.6282	27.28	6.12	1.0140	16.2
9.65	.6433	29.67	9.20	.9545	11.0
16.22	.6583	28.30	15.25	.8788	7.5
26.76	.6685	26.15	21.55	.8392	4.7
34.08	.6721	24.73	30.60	.8041	3.1

TABLE VI
Densities of Saturated Solutions

Lithium (70)		Sodium (75)		Potassium (75)	
Temp., °C.	Density	Temp., °C.	Density	Temp., °C.	Density
		−31.6	0.576	−33.3	0.625
19	.477	−33.3	.578	−39.0	.627
−80	.495	−40.7	.581	−41.0	.629
		−47.0	.585	−46.4	.636
		−51.0	.587	−49.6	.638

Bingel (8) observed that the volume of a metal solution may be approximately represented by an equation of the type

$$V = V^*n_0 + cn_1 \tag{5}$$

where n_0 and n_1 are the number of moles of ammonia and metal, respectively; and V^* and c are constants to which he gave theoretical significance. The constant c was identified with the molar volume of metal in concentrated solution, and V^* was considered the effective molar volume of ammonia. The quantity V^* was found to differ from the molar volume of pure ammonia because of change in the nature of the metal species with dilution. Obviously, equation 5 is invalid for dilute solutions.

B. APPARENT VOLUME OF THE ELECTRON IN DILUTE SOLUTIONS

Stosick and Hunt (160) have found the apparent molar volume for sodium at −44.5° and at $10^{-2}M$ to be about 59 cc. This corresponds to a volume increment of 36 cc. for the dissolution, in good agreement with the value for the most dilute solution in Table V.

Lipscomb (120), using an apparent molar volume of 67 cc. (111 $A.^3$ per atom) for sodium in dilute solution, has estimated apparent volumes of −32 and 143 $A.^3$ for Na^+_{am} and e^-_{am}, respectively. The present author has estimated the volumes of these species somewhat differently; the detailed calculations follow.

The density data of Johnson and Martens (72) have been used to calculate the following apparent molar volumes at infinite dilution: KI, 28 cc.; NaI, 20 cc.; LiI, 13 cc.; NaBr, 8 cc.; NaCl,

−2 cc. By making the assumption that K^+_{am} and Cl^-_{am} have the same volumes, we estimate the individual volumes: K^+, 3 cc.; Na^+, −5 cc.; Li^+, −12 cc.; I^-, 25 cc.; Br^-, 13 cc.; Cl^-, 3 cc. Taking 59 cc. as the apparent molar volume of $Na^+_{am} + e^-_{am}$, we estimate an apparent volume of 64 cc. for the electron (106 $A.^3$ per electron). Using these data, we calculate apparent molar volumes at infinite dilution of 52 cc. and 67 cc. for lithium and potassium, respectively. The corresponding volume increments (ΔV) of 39 cc. and 22 cc. are not unreasonable when compared with the values in Table V.

The volume associated with an NH_3 molecule in liquid ammonia at −33° is 41 $A.^3$, so it appears that the electron displaces two to three NH_3 molecules, corresponding to a cavity of radius about 3 A.

C. MOLAR VOLUMES IN THE SATURATED SOLUTIONS

Following the analogy of Pitzer (cf. Section II-B), the eutectic point of a metal–ammonia system corresponds to the triple point of the pseudometal. From the data in Tables II, III, and VI, we estimate molar volumes of 146, 173, and 164 cc. for $Li(NH_3)_4(l)$, $Na(NH_3)_5(l)$, and $K(NH_3)_5(l)$, respectively, at the eutectics. When one considers that the radii of the ammoniated ions (e.g., $Li(NH_3)_4^+$) are much larger than the ionic radius of cesium, and that molten cesium possesses a molar volume of 72 cc. at its freezing point (131), then these molar volumes seem quite reasonable.

D. COMPRESSIBILITIES

Maybury and Coulter (128) determined adiabatic compressibilities (β_s) by a sound velocity method for solutions of potassium iodide, lithium, sodium, and calcium. The compressibility of the potassium iodide solution decreases with increasing concentration (cf. Fig. 3) in a manner typical of electrolytic solutions (54). However, the compressibilities of the metal solutions increase rapidly with increasing concentration (cf. Fig. 3). This increase in compressibility is to be associated with an approach to metallic character. The alkali metals, for example, are among the most compressible of all substances (68). It is noteworthy that the compressibility of the calcium solution is much less than that for the alkali metal solutions at the same concentration; this behavior is attributable to the fact that calcium has two valence electrons, rather than one.

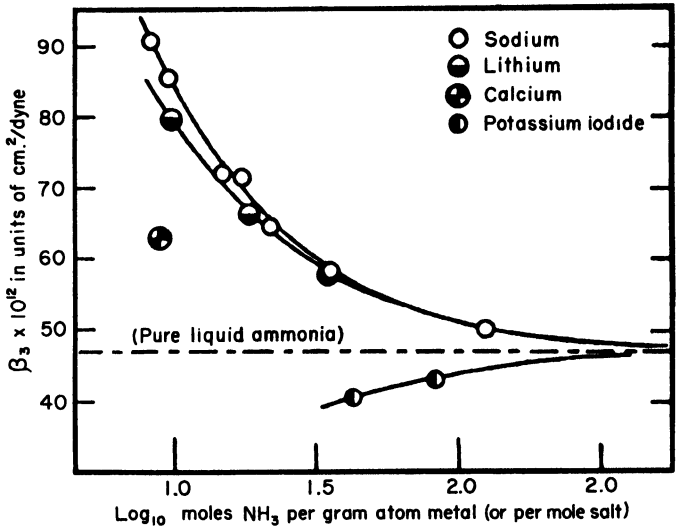


Fig. 3. Compressibilities of liquid ammonia solutions (128; reproduced by permission).

V. Magnetic Properties

A. MAGNETIC SUSCEPTIBILITIES

Kraus explained certain physical properties of sodium–ammonia solutions in terms of equilibria among sodium atoms, sodium ions, free electrons, and solvated electrons. If these were the only species

TABLE VII
Molar Susceptibilities of Sodium–Ammonia Solutions
(Measured in Static Fields)[a]

Mole ratio, NH_3/Na	$\chi \times 10^6$	
	238°K.	198°K.
60,000	1550	1200
30,000	1500	900
10,000	1100	450
920	240	0
100	25	−30
6.6	74	+70

[a] Taken from a smoothed curve through data of Huster (63).

TABLE VIII
Molar Susceptibilities of Metal Solutions
(Measured in Static Fields (47))

240°K.		220°K.	
Molarity	$\chi \times 10^6$	Molarity	$\chi \times 10^6$
Potassium			
0.00341	1268	0.00354	809
.00406	1240	.00422	790
.00812	974	.00844	488
.0318	402	.0331	232
.482	29.9	.500	−7.7
Cesium			
.00415	1130	.00432	755
.00582	1245	.00605	1020
.00690	1013	.00718	657
Calcium			
.00244	1140	.00255	978
.0100	938	.0105	271
Barium			
.00106	2280		

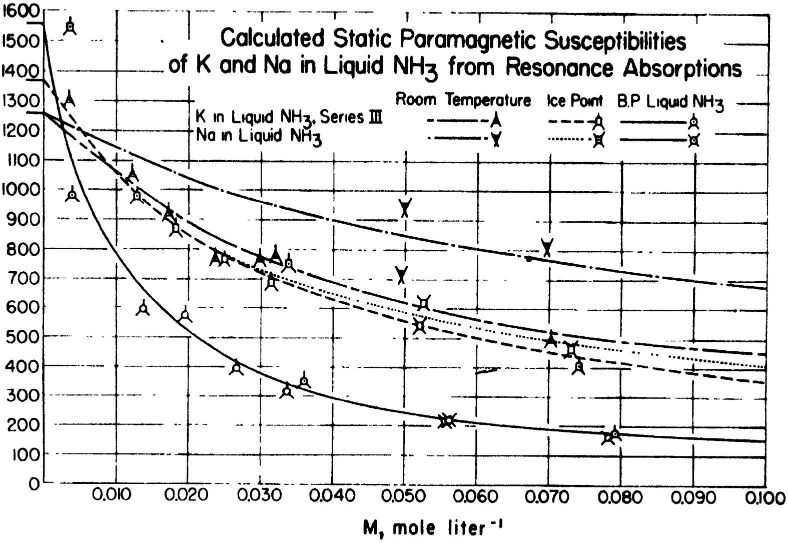
in solution, and the electrons did not interact with one another, one would expect the molar magnetic susceptibility of sodium–ammonia solutions to be independent of concentration. However, the results of magnetic susceptibility measurements for various metals (cf. Tables VII and VIII and Figs. 4 and 5) show that the molar susceptibility decreases with increasing concentration. Thus this theory cannot be correct in some major respects.

The observed variation of susceptibility with concentration is qualitatively what would be expected for a free electron gas with degenerate energy levels. At high concentrations, such electrons would constitute a degenerate Fermi gas with most of the electrons paired and not contributing to the paramagnetism. At low concentrations, the degeneracy would be removed, with a corresponding rise in the susceptibility. The molar susceptibility would decrease with increasing temperature. The following equations apply to the limiting cases of high concentration and low concentration. At high concentrations (or low temperatures),

$$\chi_m = \mu_0^2[12(\pi/3)^{2/3}N^{1/3}V^{2/3}m/h^2 - (64\pi^4/9)V^2m^3k^2T^2/Nh^6] \quad (6)$$

At low concentrations (or high temperatures),

$$\chi_m = N\mu_0^2/kT \quad (7)$$



g. 4. Calculated static paramagnetic susceptibilities of potassium and sodium in liquid ammonia from resonance absorptions (0–0.1M) (65; reproduced by permission).

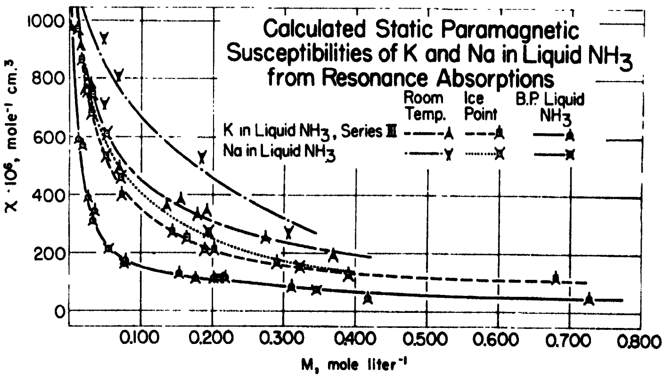


Fig. 5. Calculated static paramagnetic susceptibilities of potassium and sodium in liquid ammonia from resonance absorptions (0–0.8M) (65; reproduced by permission).

Here V is the volume available to one mole of electrons; m is the electronic mass; and μ_0 is the magnetic moment of the electron; the other symbols have their usual significance. Unfortunately, the observed susceptibilities are not in quantitative agreement with the predictions for a free electron gas. Although, at very low concentrations, the susceptibilities *approach* that for a mole of spins ($N\mu_0^2/kT$), at finite concentrations the observed susceptibilities are considerably lower than those calculated for a free electron gas. Also, the observed susceptibilities increase with increasing temperature (presumably at infinite dilution the reverse would be true, but no observations have been made beyond the crossover point). In order to explain these facts, various models have been proposed.

Huster (63) suggested an equilibrium between sodium ions, electrons, and diatomic molecules.

$$Na_2 = 2\,Na^+ + 2\,e^-_{am} \tag{8}$$

Sugarman (174) has used a similar explanation for potassium; the greater accuracy of the potassium data permits equilibrium constants to be calculated for the corresponding reaction. Becker, Lindquist, and Alder (2) have elaborated upon this theory. In particular, they propose that the diatomic molecule (M_2) consists of two ammoniated metal ions bound together by a pair of electrons which circulate on the protons of the coordinated ammonia molecules. They also emphasize the existence of a monomer species (M), namely, an ammoniated metal ion with an electron distributed on the protons of the coordinated ammonia molecules. Thus the following equilibria were considered:

$$M = M^+ + e^-_{am} \qquad K_1 = (M^+)(e^-_{am})/(M) \tag{9}$$

$$2\,M = M_2 \qquad K_2 = (M_2)/(M)^2 \tag{10}$$

The equilibrium constants were determined from Hutchison and Pastor's (65) data on the variation of susceptibility with concentration of potassium at three different temperatures (cf. Table IX). According to the constants in Table IX, the monomer species is never of much importance. In fact, at 240°K., the calculated percentage of potassium in the monomeric form at $4.5 \times 10^{-3}M$ (the concentration where the percentage of monomer is at its maximum) is only 5.9%. Therefore, an equilibrium such as given in equation 8 is more appropriate. From the temperature dependence of K_2 one calculates $\Delta H^\circ \approx -9$ kcal./mole for equation 10.

TABLE IX
Equilibrium Constants for Potassium as Calculated by Becker, Lindquist, and Alder (2)

Temp., °K.	K_1	K_2
298	0.02	100
274	0.05	900
240	0.03	9800

Freed and Sugarman (47) proposed that there are pairwise interactions between electrons similar to those which lead to the F' centers in crystals in which two electrons are trapped in a single vacancy. This theory has been elaborated by Ogg (135,137,138), Hill (57), Lipscomb (120), and Kaplan and Kittel (86). It is proposed that individual electrons are trapped in cavities which they create in the solution and are in equilibrium with pairs of electrons (antiparallel spins) similarly trapped:

$$2\,e^-_{\text{am}} = e_2{}^{2-}{}_{\text{am}} \qquad (11)$$

The electrons associated with cavities may be thought of as in molecular orbital states on the protons of the NH_3 molecules adjacent to the cavities. From the temperature coefficient of the magnetic susceptibility, Kaplan and Kittel calculate $\Delta H° = 4.6$ kcal./mole for equation 11.

Landau (110,133) pointed out that an electron can "dig its own hole" in a crystal lattice by displacement (polarization) of the neighboring ions. Pekar (145) and Davydov (28) extended this concept to "homogeneous" and polarizable dielectric media and called the electron surrounded by a polarized medium a "polaron." The "polaron" is thus synonymous with the "electron in a cavity" previously described. Deigen (29,30,32) considered the electrons as existing as "polarons," F centers, and F_2 centers. He calculated the concentrations of these species as a function of concentration and found good agreement with the observed susceptibility data.

Bingel (8) has proposed that the electron pairs react with metal ions to form "metallide" ions:

$$M^+ + e_2{}^{2-}{}_{\text{am}} = M^- \qquad (12)$$

From susceptibility data, he calculated $\Delta H° = -1$ kcal./mole for equation 11 and $\Delta H° = -4$ kcal./mole for equation 12.

B. PARAMAGNETIC RESONANCE ABSORPTION

Exploratory studies of paramagnetic resonance absorption in metal-ammonia solutions were made by Hutchison and Pastor (66), Garstens and Ryan (49), Levinthal, Rogers, and Ogg (117), and Beeler and Roux (3). Hutchison and Pastor's more complete study (64,65,67) has been the subject of a paper by Kaplan and Kittel (86).

One of the questions on which light is shed by results of the paramagnetic resonance absorption experiments is that concerning the diamagnetism of the solutions. In static field experiments the sum of the diamagnetic and paramagnetic susceptibilities is measured. Paramagnetic resonance gives just the paramagnetic part of the susceptibility. The difference between the radiofrequency and static susceptibilities at ca. $0.5M$ is 26×10^{-6}, corresponding to an r.m.s. radius of 3.0 A. for the electron's distribution in the cavities in which pairs are trapped (65). This is in good agreement with the previously estimated (cf. Section IV-B) radius for traps containing single electrons.

The spectroscopic splitting factor, g, is observed to be 2.0012 for potassium over a wide range of concentration, whereas the free electron value is 2.0023. The Δg value is comparable to those found for electrons in alkali halide F centers (86).

The paramagnetic resonance line for potassium-ammonia solutions ($\sim$0.03 gauss) is the sharpest yet reported for a liquid or solid. Kaplan and Kittel (86) suggest that the line width is caused by motionally narrowed hyperfine interactions of the unpaired electron with the protons which border the vacancy. On this basis, one would expect the line width to be inversely proportional to the frequency of rotational dipolar relaxation for ammonia, which frequency is, in turn, inversely proportional to the viscosity. Indeed, it has been found that the line width varies in direct proportion to the viscosity as the temperature is changed (118).

Electron spin resonance studies of frozen metal-ammonia systems have been made as a function of temperature (43,118). It has been concluded that, when metal–ammonia solutions are frozen, the metal precipitates out as small particles.

C. NUCLEAR MAGNETIC RESONANCE

Knight (1,90) observed that the nuclear magnetic resonance signals from metallic specimens (both solid and liquid) occurred at higher field strengths than for the same nuclear species in nonmetallic specimens. These shifts are caused by the magnetic interaction of the nuclei with the conduction electrons near the top of the Fermi distribution. McConnell and Holm (123) have determined the Knight shifts of the N^{14} and Na^{23} nuclear magnetic resonances for sodium–ammonia solutions. Unfortunately, sensitivity difficulties limited their observations to sodium concentrations greater than $NH_3/Na = 1000$. They discussed their results in terms of the average hyperfine contact densities of N^{14} and Na^{23} at an unpaired electron, $P(N^{14})$ and $P(Na^{23})$. These functions were estimated from the known potassium–ammonia paramagnetic susceptibility data and the Knight shifts. For $NH_3/Na \approx 100$, they found $P(Na^{23}) \approx 4 \times 10^{-3} P^\circ(Na^{23})$, where $P^\circ(Na^{23})$ is the contact density at an isolated sodium atom. McConnell and Holm concluded that in this concentration range, the odd electrons move in highly expanded orbitals about Na^+ ions similar to those in P-doped silicon. At sodium concentrations greater than $NH_3/Na = 50$, $P(Na^{23})$ increases rapidly, suggesting incipient metallic behavior. For all concentrations they found $P(N^{14}) \approx 0.1P^\circ(N^{14})$.

McConnell and Holm found the proton Knight shifts too small to detect; therefore they doubted that the odd electron orbitals are concentrated around protons. However, Pitzer (147a) has suggested that since the unpaired electron density on the nitrogen nuclei is substantial, the wave function must pervade the ammonia molecules. He explains the absence of a Knight shift for the protons by postulating a node in the wave function at these nuclei. This could easily arise if the odd electron orbitals are $3s$-like for nitrogen with the outer node at the N–H bond radius. Such orbitals would be $2p$-like in the vicinity of the proton.

The nuclear magnetic resonance of a frozen sodium–ammonia solution was found to be characteristic of metallic sodium, indicating that the sodium had precipitated out during the freezing (118).

Overhauser (143) predicted that saturation of the electron spin resonance in a metal should cause a large increase in the nuclear polarization because of magnetic hyperfine interaction between the unpaired electrons and the nuclei. Carver and Slichter (18) verified this prediction for both metals and sodium–ammonia solutions. For sodium solutions (concentrations 0.01, 0.4, and $0.9M$) the enhancement of the proton resonance signal was found to be proportional to the saturation factor. The line width was found to be roughly proportional to the square root of the sodium concentration, in agreement with the mass action law.

VI. Electrical Conductivity

A. TRANSFERENCE NUMBERS

When a sodium solution is electrolyzed with a d.c. current between two inert electrodes (e.g., platinum electrodes), the blue color of the anode compartment grows less intense, while the color of the cathode compartment deepens perceptibly. When a potassium amide solution is similarly electrolyzed, gas is evolved at the anode and a blue color appears at the cathode. Kraus (94) correctly deduced from such experiments that, in a metal solution, the positive electrolytic carrier is the metal ion and that the negative carrier is the blue ammoniated electron. By measuring the electromotive force of concentration cells of sodium–ammonia solutions, Kraus (95) determined the transference numbers for different concentrations. The ratio of the electron's transference number to the sodium ion's transference number varies from a limiting value of about 7 in dilute solutions to a value of 280 at ca. $0.9M$. The equivalent conductance of the sodium ion is 130 (98); thus the equivalent conductance of the dilute metal solution is calculated to be 1040. As may be seen from Figure 6, this is very close to the directly observed limiting conductance.

B. EQUIVALENT CONDUCTANCES

Metal–ammonia solutions are extremely good conductors of electricity; at all concentrations the equivalent conductances are greater than those found for any known electrolyte in any known solvent. The equivalent conductances, Λ, for lithium, sodium, and potassium are plotted against the dilution, $\log_{10} V$, in Figure 6. Literature references to conductivity studies are listed in Table X. The conductances for concentrated solutions (for which the values could not be plotted on the graph) are extremely high and of the same order of magnitude as found for metals. For example, the specific conductance of a saturated sodium solution at −33.5° is 5047 mhos; that for mercury at 0° is 10,600 mhos (102). The *equivalent* conductance of sodium in the saturated solution is 1.016×10^6 mhos

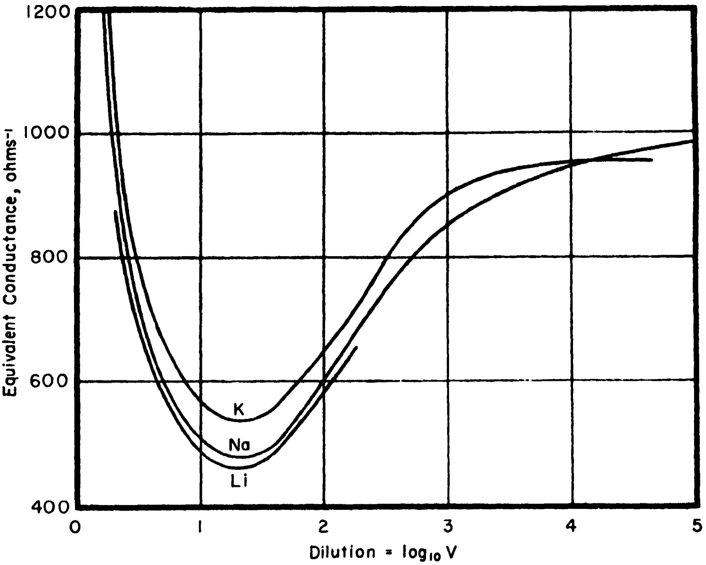


Fig. 6. Equivalent conductance of metal–ammonia solutions at −33.5°. V = liters of pure ammonia of density 0.674 in which one gram atom of metal is dissolved (174; data from ref. 96).

(126); the *equivalent* conductance of mercury is 0.156 × 10^6 mhos. With increasing dilution the equivalent conductances fall and reach minimum values at approximately 0.05*M*. At high dilutions the conductances asymptotically approach values which are some seven times as large as equivalent conductances of salts in water.

In the dilute region, metals appear to be similar to strong electrolytes in ammonia. Kraus (97) interprets the conductivities as being of an electrolytic nature and involving the formation of ion pairs. For example, he calculates a dissociation constant for Na^+e^- of 0.05 at −33°, which corresponds to 85% dissociation at 0.01*M*. However, the data can probably be just as well explained by an equilibrium such as equation 8.

C. TEMPERATURE COEFFICIENT OF CONDUCTIVITY

The temperature coefficients of the conductivity of metal–ammonia solutions are very unusual. Kraus and Lucasse (103,105) determined

TABLE X

Conductance Studies in Liquid Ammonia

Temp., °C.	Molarity range	Ref.
	Lithium	
−33	0.0055 to 2.4	96
−38 to −70	2.25	60
	Sodium	
−33	0.000023 to 2.0	96
−33.5	0.60 to satd.	102
−33.5	0.00018 to 0.78	51
−48.5	0.00048 to 0.29	51
−70.0	0.00055 to 0.49	51
−35 to −75	$\sim 10^{-5}$	135
−90 to −180	"frozen solns."	13,27,37,52,59,60, 85,122,134,136, 140,162,168
	Sodium + potassium (Na/K = 1.46)	
−33	0.000067 to 0.86	96
	Potassium	
−33	0.000102 to 0.6	96
−33.5	1.4 to satd.	102
−33.5	0.00020 to 0.26	51
−48.5	0.00039 to 0.18	51

the coefficients for sodium and potassium as a function of concentration. In dilute solutions the coefficients,

$$\Delta K/\Delta t \times 100/K_{-33.5}$$

have values around 1.9% per degree. With increasing concentration the temperature coefficients for sodium and potassium increase, passing through maximum values of 3.6 and 4.55% per degree at concentrations of 0.87 and 1.10*M*, respectively. These maxima correspond to activation energies around 0.2 electron volt, which is not an unreasonable energy gap for a semiconductor (89). On going to more concentrated solutions the coefficients fall rapidly, almost becoming negative. The coefficients for saturated solutions of sodium and potassium are 0.066 and 0.044% per degree, respectively. The corresponding coefficient for molten sodium or molten potassium is about −0.3% (131).

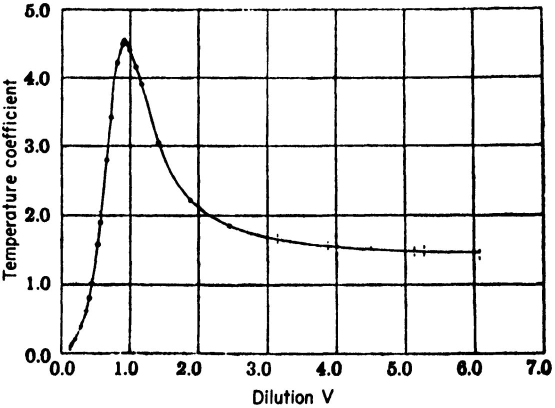


Fig. 7. Temperature coefficient of conductivity for potassium–ammonia solutions (105; reproduced by permission).

D. WIEN EFFECT

In measurements of the Wien effect in solutions of alkali metal–ammonia solutions at −78°, it was found that a 4% rise in conductivity could be achieved with fields of magnitude 15,000 volts/cm. (115). In aqueous solutions of electrolytes, fields of the order of 100,000 volts/cm. are required to obtain comparable effects. The abnormally strong effect in metal–ammonia solutions may be associated with the "falling" of the electron to a conduction level in the solvent.

E. CONDUCTION MECHANISM IN DILUTE SOLUTIONS

At least three conduction mechanisms have been considered for dilute solutions. A common concept is that the electrons are solvated and that they move in the form of $(NH_3)_n^-$ ions. However, the observed ionic conductivities do not support this concept. From Table XI we see that the conductivity of the electron is abnormally high (some four or five times as great as would be expected for an ion its size). Thus, it seems unlikely that the electron and its shell of solvated ammonia moves as an entity. In fact, Kaplan and Kittel, using Stokes' law, have calculated that an ion of radius 3 A. would have a mobility one-tenth that observed for the electron (however, they considered this good enough agreement to support the ionic

TABLE XI

Some Ionic Conductances in Liquid Ammonia at −33.5° (98)

Ion	Conductivity, cm.²/ohm/equiv.
Li^+	112
Na^+	130
NH_4^+	131
I^-	171
Cl^-	179
e^-_{am}	910 (95)

conductance concept). It has been observed for many aqueous electrolytes that the product of the solvent viscosity and the equivalent conductance is approximately independent of temperature (54). However, the temperature coefficient of resistance for dilute metal solutions is about −1.9% per degree as compared with the temperature coefficient of viscosity for ammonia of only −1.1% per degree (97). Thus, again, we conclude that viscosity is not the only factor which influences the conductivity of dilute metal solutions.

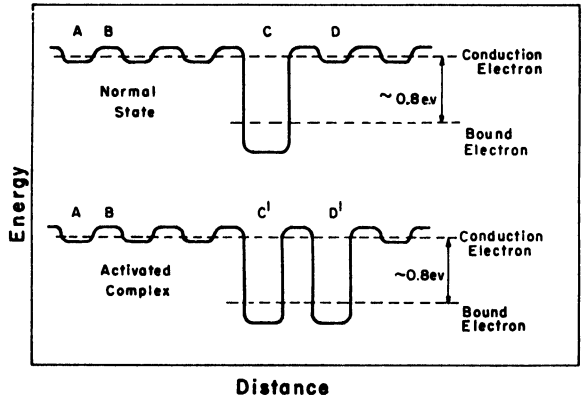


Fig. 8. Model of dilute metal–ammonia solution.

Some consideration has been given to a semiconductor concept. Here conduction presumably takes place by thermal activation of the electron to a conduction band located about 0.8 e.v. above the trapped electron level (see Section VIII for the evidence leading to this choice of energy). However, the observed temperature coefficient of the conductivity is in complete disagreement with the predicted temperature coefficient (~16% per degree).

Dewald and Lepoutre (35), on the basis of the thermoelectric properties of metal–ammonia solutions (Section IX), suggest a quantum "tunnel" mechanism. We shall present this concept with considerable amplification and elaboration because it seems to explain the facts most adequately. Consider the potential energy diagram in Figure 8. In liquid ammonia, not all sites are equally favorable for an electron. There are sites *B*, such as the electron clouds around nitrogen atoms, where the potential energy of an electron is somewhat greater than it is at sites *A*, such as the neighborhoods of the protons. We shall define a conduction electron as an electron which pervades the entire solution; thus the ammonia dipoles do not move to "follow" a conduction electron. If such an electron remains in the vicinity of a potential minimum (such as *A*) long enough, it "burrows" itself a cavity, *C;* that is, the neighboring ammonia molecules orient themselves favorably, and two or three ammonia molecules are pushed away. Alternatively, potential minima of depths intermediate between *A* and *C* exist in liquid ammonia because of the randomness of the solvent, and these may "trap" conduction electrons with subsequent rearrangement and enlargement of the sites.

Ordinarily, there is only a small electron density at site *D*. However, because of thermal motions of the ammonia molecules in the vicinity of sites *C* and *D*, these two sites will occasionally be equally favorable for occupancy by the electron (sites *C′* and *D′*). This situation amounts to a transition state for the diffusion of the electron from left to right in the solution. The net diffusion of an electron from site *C* to site *D* involves the movement of only two or three ammonia molecules from site *D* to site *C*, the relaxation of the ammonia molecules surrounding site *C*, and the orientation of ammonia molecules around site *D*. Thus the rate of diffusion of an electron through ammonia is partly limited by the rate of diffusion of two or three ammonia molecules; this process should be much faster than the diffusion of ordinary ions which carry with them shells of coordinated ammonia molecules. If an electric field is applied across the solution, migration of the electron will be more favorable in one direction than another. Since the activated complex is achieved by both the diffusion of ammonia molecules and by the orientation of ammonia molecules, it is reasonable that the temperature coefficient of conductivity be somewhat higher than that for a simple diffusional process.

Connick (21) has suggested that this conduction mechanism be described in terms of an "amoeba" electron. Whereas an ordinary ion (e.g., chloride ion) has a fairly rigid spherical shape, the electron is easily deformed from a spherical shape and thus may flow more easily through a solution.

F. CONDUCTION MECHANISM IN CONCENTRATED SOLUTIONS ($>0.1M$)

Deigen (33) has suggested that in the region of the maximum in the conductivity temperature coefficient, the conductivity proceeds by passage of electrons from colloidal metal particles to the ammonia dielectric. However, there is very little evidence (107) in favor of the colloidal hypothesis.

Farkas (42) has explained the conductivity of sodium solutions from 1 to $5M$ by quantum mechanical jumps of electrons between metal atoms. The following expression was derived for the equivalent conductance:

$$\Lambda = (3 \times 10^{14}/I^{1/2}C) \times 10^{-4\cdot 2} \times 10^{6}I^{1/2}C^{-1/3} \qquad (13)$$

where Λ is the equivalent conductance; C is the concentration in moles per liter; and I is the barrier height, or ionization potential, for sodium. If a value of about 7×10^{-13} erg (0.4 e.v.) is used for I, the theory is in fair agreement with experiment in the concentration range 1–$5M$.

The present author believes that the minimum in the equivalent conductance curve and the maximum in the temperature coefficient curve may be explained in terms of the gradual decrease in energy of the conduction electron with increasing concentration. At high concentrations of metal, the fraction of the valence electrons which are unpaired and which exist in cavities of type C (Fig. 8) is very small. Most of the electrons are being used to bind together groups of metal ions to form relatively immobile species, such as M_2, M_3, M_2^+, and M_3^-. Thus the equivalent conductivity at ca. $0.1M$ is very low. However, consider the electrons associated with the metallic clusters. Species such as M_2 and M_3^- represent "filled" electron sites, and

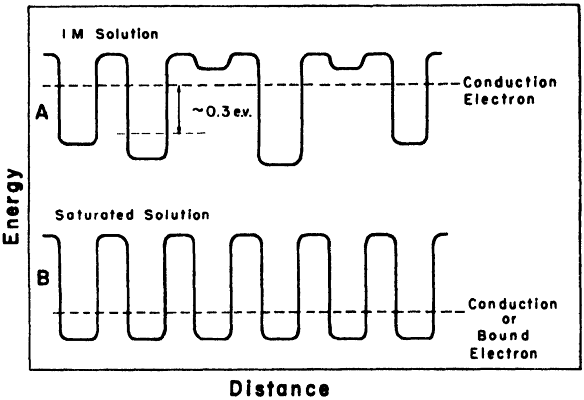


Fig. 9. Models of concentrated metal–ammonia solutions.

species such as M_2^+ and M_3 represent "vacant" electron sites. At concentrations less than about 1*M*, the "filled" and "vacant" sites are too widely separated to permit quantum tunneling. However, at concentrations near 0.1*M*, the average separation between "vacant" sites is sufficiently small that the energy of the conduction electron is considerably reduced from its value in dilute solutions. Then an appreciable amount of conductivity occurs by thermal exitation of bound electrons to this conduction level (see Fig. 9A). As the metal concentration increases, this energy gap decreases. Therefore, as the metal concentration increases beyond 0.1*M*, this "conduction band" conductivity more than compensates for the decrease in "cavity" type conductivity, and the equivalent conductance rises. In the range 0.1–1*M*, the conductivity is of two types; but around 1*M* the conduction band conductivity predominates (as shown by the maximum in the temperature co-efficient curve).

In the saturated solution, the electron sites are more regularly spaced and very close to one another (Fig. 9B). The conduction electron has become practically identical with the bound electron; thus the temperature coefficient of conductivity is essentially zero. The electrons are so mobile that the individual sites have lost their identities, all the potential wells have practically the same depth.

It is obvious that, in the very concentrated solutions, conductivity may occur both by excitation of electrons to the conduction level and by quantum tunneling from the bound state.

VII. Thermodynamics

A. THERMOCHEMISTRY

The heats of solution of the alkali metals other than lithium are very small or zero, whereas lithium and the alkaline earth metals dissolve with evolution of large amounts of heat. (It will be remembered that this latter group of metals, in contrast to the former, either form, or show a tendency to form, stable solid ammoniates.) From Table XII we see that the heats of solution refer to concentrations around 0.1*M*, where the electron spins are practically completely paired. Coulter and Candela (17) have measured the heat of dilution of potassium from ca. 0.1*M* to "infinite dilution" as 3 kcal./mole, and they write

TABLE XII
Heats of Solution of Metals in Ammonia at −33°

Metal	Concentration, *M*	$\Delta H°$, kcal./mole	Ref.
Li	0.067	−9.65	25
Na	0.4	+1.4	106
K	0.07	0.0	106,157
Rb	0.13	0.0	157
Cs	0.19	0.0	157
Ca	0.023	−19.7	172
Sr	—	−20.7	23,171
Ba	—	−19.0	23,171

$$\frac{1}{2}\, e_2{}^{2-}{}_{\text{am}} \longrightarrow e^-{}_{\text{am}} \qquad \Delta H° = 3 \text{ kcal./mole} \tag{14}$$

This value is in rough agreement with the values 2.3 and 4.6 kcal. estimated by Kaplan and Kittel (86) and Becker, Lindquist, and Alder (2), respectively, from the temperature coefficient of the magnetic susceptibility.

The heats of reaction of various metal solutions (ca. 0.1*M*) with ammonium salt solutions are given in Table XIII. It will be noted that the values are all very close to −40.1 kcal. per equivalent of metal. Coulter (23) has interpreted this fact as an indication that the *net* reactions are all indentical, and he writes

$$\frac{1}{2}\, e_2{}^{2-}{}_{\text{am}} + NH_4{}^+ = NH_3 + \frac{1}{2}\, H_2 \qquad \Delta H° = -40.1 \text{ kcal./mole} \tag{15}$$

This conclusion is not strictly valid if one recognizes that the electron pairs are associated with cations. However, we can state that the over-all heat of dissociation and unpairing is approximately the same for all metals, namely, about 3 kcal. per electron. We shall take 40 kcal./mole as the heat of formation of $e_2{}^{2-}{}_{\mathrm{am}}$ and 43 kcal./mole as the heat of formation of $e^-{}_{\mathrm{am}}$.

The heat of ammonation of an electron (i.e., the total heat evolved upon immersing a gaseous electron in liquid ammonia) is a quantity of considerable theoretical interest. Unfortunately, there is no way to measure this quantity. Most methods used for estimating individual ionic solvation heats involve schemes for apportioning the heats of solvation of pairs of plus and minus ions.

TABLE XIII
Heats of Reaction of Metal Solutions with Ammonium Salt Solutions in Liquid Ammonia at −33°

Metal	$\Delta H°$, kcal./equiv.	Ref.
Li	−40.8	25
Na	−40.0	24
K	−39 7	24
Cs	−41.6	24
Ca	−39.8	172
Sr	−40.0	23,171
Ba	−42.5	23,171

Coulter (23), using a highly simplified model, calculated theoretical ammonation heats as a function of ionic charge and ionic radius. For Na^+ and Br^- he calculated heats of 130 and 51 kcal./mole, respectively. Therefore he divided the experimental ammonation heat for the Na^+–Br^- pair in the ratio 130:51 and thus obtained fair agreement between calculated and "experimental" ammonation heats for a number of ions. He calculated an ammonation heat for the electron $\Delta H° = -11$ kcal./mole. This value seems much too positive when compared with the experimental photoelectric threshold energy of 33 kcal./mole (Section VIII-C). The hydration heats of the rubidium ion and the bromide ion have been estimated to be nearly identical (15). Let us assume that their ammonation heats are also identical. Since $\Delta H°_f = 63$ kcal./mole for $Rb^+{}_g + Br^-{}_g$

(111), and $\Delta H°_f = -98$ kcal./mole for $Rb^+_{am} + Br^-_{am}$ (113), we calculate

$$Br^-_g \longrightarrow Br^-_{am} \qquad \Delta H° = -80 \tag{16}$$

This latter heat may be combined with the conventional $\Delta H°_f$ for the electron in ammonia (43 kcal./mole), the conventional $\Delta H°_f$ for Br^-_g (-55 kcal./mole (111)), and the conventional $\Delta H°_f$ for Br^-_{am} (-59 kcal./mole (113)) to yield

$$e^-_g \longrightarrow e^-_{am} \qquad \Delta H° = -39 \text{ kcal./mole} \tag{17}$$

From a comparison of heats of formation for species in water and in ammonia, it has been concluded that ammonation heats are 5 kcal./mole more negative than hydration heats (79). Brewer *et al.* (15) give $\Delta H° = -74$ kcal./mole for the hydration heat of Br^-, indicating an ammonation heat of -79 kcal./mole (fortuitously close to our previous estimate). Latimer (111) gives -81 kcal./mole for the hydration energy of Br^-, indicating an ammonation heat of -86 kcal./mole. Either value will yield an ammonation energy for the electron close to our previous value of -39 kcal./mole. It will be appreciated that the limits of confidence for this value are about ±10 kcal./mole.

Ogg estimated the ammonation energy of the electron by considering the energy of an electron confined to a spherical box (141). If the dielectric constant of the medium is assumed to be infinite, the Born relation gives us the expression $-e^2/2r_0$ for the potential energy of an electron in a hole of radius r_0. This energy would become enormous if r_0 were permitted to approach zero, but the Uncertainty Principle would be violated. The Schrödinger equation yields the expression $h^2/8mr_0^2$ for the kinetic energy of the electron confined to the spherical box. Thus the total energy is

$$W = h^2/8mr_0^2 - e^2/2r_0 \tag{18}$$

By minimizing W, one calculates $W = -0.38$ e.v. and $r_0 = 9.9$ A. This type of calculation has been refined by taking account of the decrease in dielectric constant in the neighborhood of the hole (120) and by considering a spherical well of finite "depth" (159). Although reasonable radii (ca. 3 A.) were obtained by adjustment of the parameters, the calculated ammonation energies were much lower than our "experimental" value. However, Jortner (82,83), using a variation method on a one-parameter wave function, has calculated an ammonation energy of 39 kcal./mole for a cavity radius of 3.0 A.

B. OXIDATION POTENTIALS

The standard oxidation potentials for some of the more electropositive metals are given in Table XIV. Some of the potentials have been obtained from galvanic cell data, others from the solubilities of metal salts. In all cases it was necessary to correct the potentials to 25° using known heats of formation.

TABLE XIV
Oxidation Potentials for Metals in Liquid Ammonia at 25° (78)

Couple	$E°$, volts
$Li = Li^+ + e^-$	2.34
$Sr = Sr^{++} + 2e^-$	2.3
$Ba = Ba^{++} + 2e^-$	2.2
$Ca = Ca^{++} + 2e^-$	2.17
$Cs = Cs^+ + e^-$	2.08
$Rb = Rb^+ + e^-$	2.06
$K = K^+ + e^-$	2.04
$Na = Na^+ + e^-$	1.89
$Mg = Mg^{++} + 2e^-$	1.74

In the electrolysis of salt solutions with a dropping mercury electrode, three cathodic reactions might possibly occur: hydrogen discharge, amalgamation of the reduced cation, and electron dissolution. Laitinen and Nyman (108) found that alkali metal ions are reduced polarographically by the amalgamation process. However, they found that, with a solution of tetrabutylammonium iodide, electron dissolution is the only cathodic process, and that the process occurs with no detectable overvoltage (109). Hence they were able to determine polarographically the oxidation potential of the ammoniacal electron:

$$e^-_{am} = e^- \qquad E° = 1.89 \text{ v. at } -36° \tag{19}$$

Using the known heat of formation of the electron, one calculates the value 1.95 v. for 25°.

By combining the oxidation potentials for the electron and a metal, one may calculate the solubility product for the metal. Thus, for

$$Na = Na^+ + e^-_{am} \tag{20}$$

$E_0 = -0.06$v. (25°) and $\Delta F_0 = 1.4$ kcal./mole. Russell and Sienko (154a) have determined $E°$ and $\Delta F°$ for reaction 20 from galvanic cell studies. They report $E° = -0.10$ v. and $\Delta F° = 2.4$ kcal./mole at −50° and $E° = -0.11$ v. and $\Delta F° = 2.6$ kcal./mole at −70°.

The entropy of the ammoniacal electron (relative to $S^0_{H^+} = 0$) is calculated to be 9 e.u. Using the approximation of Latimer and Jolly (113), we calculate 34 e.u. as the absolute entropy.

It is remarkable that, at 25°, $K = 10^{-6}$ for the reaction

$$^1/_2\,H_2 + NH_2^- = e^-_{am} + NH_3 \qquad (21)$$

If the reaction were reversible, one would expect that hydrogen (at 100 atmospheres pressure) would be in equilibrium with a solution $1M$ in NH_2^- and $10^{-5}M$ in e^-_{am}. Such a solution would be pale blue.

VIII. Photo Processes

A. ABSORPTION SPECTRA

1. *Absorption Spectra of Liquid Solutions*

The blue color of dilute metal solutions in liquid ammonia is due to the short wavelength tail of a very broad and intense absorption band whose peak occurs at approximately 15,000 A. (12,80,163). The available evidence indicates that, at least in dilute solutions, the spectra for the various metals are identical.

Metal solutions in amines and ammonia-amine mixtures are characterized by two absorption peaks, one in the infrared (~15,000 A.) and the other in the visible (~6500 A.) (12,45,50,62). Blades and Hodgins (12) attribute the existence of two bands to the variation in physical arrangement of the solvent molecules around the electron cavities. They attribute the infrared absorption to cavities with protons oriented inward, and the visible absorption to cavities with hydrocarbon groups oriented inward. It is difficult to see why there should be two distinct absorptions, when all possible intermediate arrangements of N—H and N—R groups around the cavity are just as likely as the two extremes postulated.

Platzman and Franck (149) suggest that the observed absorption bands are part of a series of transitions. This theory does not explain why a change in temperature favors one band at the expense of the other.

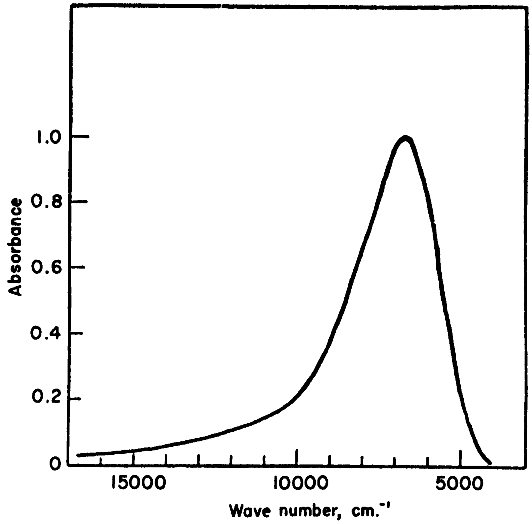


Fig. 10. Absorption spectrum of potassium–ammonia solution (12; reproduced by permission).

Fowles, McGregor, and Symons (45) suggest that the infrared and visible bands are caused by $e^-{}_{\mathrm{am}}$ and $e_2{}^{2-}{}_{\mathrm{am}}$, respectively. This theory is unacceptable for alkali metal–ammonia solutions, because no absorption peak has ever been observed in the visible range in such solutions. In fact, recent studies have shown that at −70° sodium–ammonia solutions are in strict accord with Beer's law for all visible wavelengths in the concentration range 0.001–0.1*M* (81). It is significant that this concentration range straddles the range where the electrons begin to pair. However, the absorption spectra of concentrated solutions in the near infrared have never been observed (primarily because of the experimental difficulty of obtaining necessarily exceedingly short cell lengths). There may be a second absorption peak at wave lengths shorter than 15,000 A.

The possibility exists that the visible peak is characteristic of amines and that the infrared peak is characteristic of ammonia. The solubility of a metal in an amine is markedly increased by the addition of small amounts of ammonia (41,132), and it is very difficult to free low-boiling amines of traces of ammonia (61).

The optical transition at 15,000 A. in ammonia solutions has been identified with an electronic transition from a 1*s* state to a 2*p* state (28,31,33,82,83). If this concept is correct, one might observe fluorescence (2*p* → 1*s* transitions).

It seems just as reasonable to correlate the absorption of light by a metal–ammonia solution with the excitation of bound electrons to the conduction level discussed in Section VI-E. The absorption peak corresponds to an excitation energy of 0.83 e.v. (19 kcal./mole), although it may be incorrect to identify this energy with the minimum energy gap between a bound electron and a conduction electron. The absorption peak is not symmetrical; the extinction coefficient drops more rapidly on the long wavelength side than on the short wavelength side (12). Perhaps the energy of the long wavelength threshold for absorption is more appropriate. It has been observed (135) that dilute sodium solutions increase in conductivity upon irradiation with visible light, but the photoconductivity threshold has not been determined.

Pitzer (148) has pointed out that, since the energy gap between the bound electron and conduction electron becomes smaller at high concentrations, the absorption peak should move toward longer wavelengths at high concentrations. Unfortunately, the absorption peak has never been measured at concentrations higher than about $0.01M$.

2. Absorption Spectra of Solid Solutions

Thin layers of solid ammonia containing small amounts lithium, sodium, or potassium metal show an absorption peak near 11,500 A. (14). Another peak (whose position is characteristic of the alkali metal) is observed in the neighborhood of 6000 A. Similar spectra have been observed for solutions of lithium and potassium in glasses of ether–isopentane–triethylamine–methylamine (119). It was observed that irradiation of these glasses with light of wavelength shorter than 5400 A. caused a bleaching of the visible peak and an intensification of the infrared peak, and that softening of the glass caused the original spectrum to reappear. It has been reported (26) that irradiation of alkali metal–ammonia films with long wave radiation greater (shorter?) than 5800 A. caused bleaching of the visible color.

These spectra have been variously interpreted in terms of electronic transitions to a series of bound levels (149), transitions characteristic of $e_2{}^{2-}{}_{\mathrm{am}}$ and $e^-{}_{\mathrm{am}}$ (45), absorption by neutral metal atoms or colloidal particles of metal (14), and excitation to a conduction band (26).

3. *Absorption Spectra of Amide and Iodide*

The maxima in the ultraviolet absorption spectra of the aqueous halide ions have been interpreted as corresponding to inner photoelectric processes (152). The energies of the transitions are consistent with the hypothesis that, in each case, the electron is ejected from the halide ion to a common energy level in the solution. It is interesting to consider in the same manner the absorption spectra of liquid ammonia solutions of the amide ion and the iodide ion (112,139).

The absorption peaks of the ammoniacal amide ion and iodide ion occur at 3410 (142) and 2540 A. (112), respectively. These wavelengths correspond to energies of 83.8 and 112.5 kcal./mole, respectively. It seems reasonable to presume that the electrons are excited to the same conduction band, as is the electron in a metal–ammonia solution. We must realize that these photo processes occur much more rapidly than the ammonia molecules reorient themselves. Thus we write the equations

$$e^-{}_{\mathrm{am}} = e^-{}_{\mathrm{cond}} + \text{“hole”} \qquad \Delta H^\circ \approx 19 \text{ kcal./mole} \tag{22}$$

$$\mathrm{NH_2}^- = e^-{}_{\mathrm{cond}} + \mathrm{NH_2}^* \qquad \Delta H^\circ \approx 84 \text{ kcal./mole} \tag{23}$$

$$\mathrm{I}^- = e^-{}_{\mathrm{cond}} + \mathrm{I}^* \qquad \Delta H^\circ \approx 112 \text{ kcal./mole} \tag{24}$$

where “hole” represents the ammonia molecules arranged as they are around a bound electron; $\mathrm{NH_2}^*$ represents an $\mathrm{NH_2}$ radical with a shell of ammonia molecules arranged as they are around an $\mathrm{NH_2}^-$ ion; and I* represents an I atom with a shell of ammonia molecules arranged as they are around an I^- ion. The ΔH° values may be in error because they correspond to the peaks of the absorption curves rather than the absorption thresholds. However, the difference between any two of the heats is probably fairly accurate because the errors in the individual heats are probably of the same magnitude and sign. Thus we write

$$\mathrm{NH_2}^- + \text{“hole”} = \mathrm{NH_2}^* + e^-{}_{\mathrm{am}} \qquad \Delta H^\circ = 65 \text{ kcal./mole} \tag{25}$$

$$\mathrm{I}^- + \text{“hole”} = \mathrm{I}^* + e^-{}_{\mathrm{am}} \qquad \Delta H^\circ = 93 \text{ kcal./mole} \tag{26}$$

Now let us consider the following two equations:

$$\text{“no hole”} + NH_2^- = NH_2 + e^-_{am} \qquad \Delta H^\circ = 70 \text{ kcal./mole} \qquad (27)$$

$$\text{“no hole”} + I^- = I + e^-_{am} \qquad \Delta H^\circ = 106 \text{ kcal./mole} \qquad (28)$$

The heats of these reactions have been estimated from thermodynamic data. The heats of formation of NH_2^- and I^- are known (71). The heats of formation of NH_2 and I have been estimated from those for $NH_2(g)$ (150) and I(g) (111), using the approximation that the heats of solution of NH_2 and I are the same as those of NH_3 (144) and Xe (46), respectively. Using the last four equations, we now readily write

$$\text{“hole”} + NH_2 = \text{“no hole”} + NH_2^* \qquad \Delta H^\circ = -5 \text{ kcal./mole} \qquad (29)$$

$$\text{“hole”} + I = \text{“no hole”} + I^* \qquad \Delta H^\circ = -13 \text{ kcal./mole} \qquad (30)$$

The heats for these reactions are the differences in relaxation energies for the shells of ammonias around an electron and an amide ion and an electron and an iodide ion. We see that the relaxation associated with the electron is more exothermic than the relaxation associated with either the amide ion or the iodide ion. This fact is very reasonable when one considers that the relaxation of a "hole" differs from the other relaxations in that it involves the transfer of two or three ammonia molecules from the surface of the solution to the hole. It is generally agreed that this process is exothermic by slightly less than two or three times the heat of vaporization of ammonia.

It should be pointed out that halide absorption spectra have been interpreted in terms of excitations to bound levels (149). Such an interpretation renders the above calculations invalid.

B. PHOTOLYSIS OF METAL SOLUTIONS

When pure liquid ammonia is exposed to light of the same spectral region which causes the decomposition of gaseous ammonia (2300 A.), no observable change is produced; but when metallic solutions are so exposed, a reaction occurs, with the production of amide ion and hydrogen (142). The quantum efficiency is found to increase regularly with the concentration of metal, but never reaches unity. The long wavelength threshold and maximum occur at 2550 and 2300 A., respectively. Ogg, Leighton, and Bergstrom (142) have interpreted these results in terms of the following principal mechanism:

$$NH_3 + h\nu \longrightarrow H + NH_2 \quad (31)$$

$$H + NH_2 + NH_3 \longrightarrow 2\,NH_3 \quad (32)$$

$$NH_2 + e^-_{am} \longrightarrow NH_2^- \quad (33)$$

$$2\,H + NH_3 \longrightarrow H_2 + NH_3 \quad (34)$$

C. PHOTOELECTRIC EFFECT

If bound electrons are excited by sufficiently energetic photons, the excited electrons will be able to leave the solution. A current of electrons flowing from the solution to an anode over the solution may then be detected (138,161). Häsing (55) found the work function for sodium solutions to vary from 1.45 e.v. (33 kcal./mole) for ca. 0.1*M* solutions to 1.60 e.v. (37 kcal./mole) for concentrated solutions. One concludes that the electrons are not bound much more tightly in concentrated solutions than in dilute solutions. Of course, just as in the excitation to the bottom of the conduction band, the solvent is left unrelaxed during the photoelectric process. Therefore the work functions are not equal to the solvation energies of the electron. However, we might expect these energies to be of the same magnitude, and it is satisfying to find that our previously estimated ammonation energy (39 kcal./mole) is in rough agreement with the work function.

D. REFLECTION

The color of the reflected light from concentrated solutions of alkali metals in ammonia shows a remarkable dependence on the angle of incidence. For a saturated lithium solution, the color changes from deep red to yellow, to green, and finally to white as the angle of incidence increases from 0 to 90 degrees (69).

IX. Miscellaneous Physical Properties

A. THERMOELECTRIC PROPERTIES (34,35,114)

If two similar electrodes are immersed in two regions of a metal–ammonia solution which are at different temperatures, a measurable electric potential will exist between the electrodes. This thermoelectric power for concentrated sodium and potassium solutions (4–12*M*) is of the order of magnitude characteristic of metals, 1–10 μvolts/degree. The thermoelectric power of these solutions increases with decreasing concentration, indicating electronic conduction.

Dilute solutions of sodium and potassium ($<0.1M$) show a large positive temperature dependence for the thermoelectric power; that is, the Thomson coefficient ($\partial^2\psi/\partial T^2$) is very large. The addition of salt also causes a large increase in the thermoelectric power. Neither these effects nor the variation of thermoelectric power with concentration may be completely explained in terms of association of the electrons and metal ions. However, all three effects have been semiquantitatively explained by assuming that the electrons move in the solution with a negative heat of transport. This led Dewald and Lepoutre (35) to a tunnel mechanism for electronic conduction. They postulate that, in making transitions from one polarization center to another, an electron leaves the dipole polarization energy of the center behind and, with the electron gone, this energy is transformed into heat. In its new environment the electron polarizes the solvent at the expense of the thermal energy of the surroundings. Thus polarization energy flows in a direction opposite to the electron flow (see Section VI-E for further discussion).

B. CLUSTER SIZE

There have been suggestions (19,107) that metal–ammonia solutions are colloidal, but the evidence does not appear to deserve serious consideration (48). On the other hand, small angle X-ray scattering from metal–ammonia solutions indicates the presence of scattering centers of dimensions of the order of 15 A., with at most a few types of centers in a given solution, and with the type of center depending on the metal ion (158). These data are in good agreement with the cluster concept elaborated in Section V-A.

C. ORTHO–PARAHYDROGEN CONVERSION (20)

The rate of conversion of parahydrogen to orthohydrogen in liquid ammonia solution is markedly catalyzed by dissolved sodium. In fact, $0.033M$ sodium gave a half-life of only 37 seconds at $-53°$. This rate is much faster than that observed in aqueous solutions of cupric ion possessing even greater paramagnetism.

D. KINETICS OF DISSOLUTION (71)

Sodium metal dissolves in ammonia with an apparent activation energy of 4.2 kcal./mole. The rate of solution increases both when the metal is made cathodic and when the velocity of a rotating metal sample is increased. These data indicate that the solution process is a diffusion-controlled electrochemical process.

E. VISCOSITY

The viscosity of sodium–ammonia solutions has been measured as a function of both temperature and concentration (88). The viscosity decreases with increasing concentration; this has been taken as evidence for the quasimetallic nature of the concentrated solutions (128).

F. HALL EFFECT

A charged particle moving through a magnetic field suffers a force perpendicular to both the field and the direction of motion. It has been observed (53) that when a dilute sodium amide solution is electrolyzed with a needle cathode, a blue streak moves from cathode to anode at a rate (at 20°) of 0.012 cm./sec. per volt/cm. A magnetic field shifts the streak in the direction corresponding to a negative charge for the blue species. The Hall constant for a frozen saturated solution of lithium in ammonia has been found to be $R = -1.38 \times 10^{-2}$ abs. e.m.u. (70). On the degenerate Fermi gas theory of free electrons the Hall constant is

$$R = -c/n_0e \tag{35}$$

where c is the velocity of light, n_0 is the concentration of free electrons; and e is the electronic charge. From the Hall constant, one calculates $n_0 = 4.53 \times 10^{21}$ electrons/cc. or 7.5×10^{-3} moles/cc. This corresponds very closely to the concentration of lithium at the eutectic, indicating that there is one free electron per lithium atom.

X. Chemical Properties

A tremendous amount of chemistry, largely synthetic chemistry. has been carried out using metal–ammonia solutions. Unfortunately, the chemical behavior of these solutions tells us little about their constitution. Therefore, in keeping with the purpose of the review, this section is very brief.

The author is unaware of any thorough kinetic studies of homogeneous reductions by metal–ammonia solutions. It would seem that such studies might yield very fascinating results. As it is, the only clues we have to the mechanisms of metal–ammonia reductions are yield data and a few fragmentary rate data.

Birch (9) has discussed the reduction of organic compounds by metal–ammonia solutions from a mechanistic point of view. He has extended the theory of electronic reduction outlined by Michaelis and Schubert (130). Watt (163–167) has summarized the reactions of metal–ammonia solutions with both inorganic and organic compounds. One may consider three initial steps: (*1*) simple electron addition without bond rupture,

$$e^-_{am} + X \longrightarrow X^- \tag{36}$$

(*2*) the breaking of a bond by the addition of one electron,

$$e^-_{am} + X{-}Y \longrightarrow X\cdot + Y^- \tag{37}$$

and (*3*) the breaking of a bond by the addition of two electrons,

$$2\,e^-_{am} + X{-}Y \longrightarrow X^- + Y^- \tag{38}$$

The following reactions are examples of electron addition reactions without bond rupture.

$$e^-_{am} + O_2 = O_2^- \tag{39}$$

$$e^-_{am} + NO_2^- = NO_2^{2-} \tag{40}$$

$$e^-_{am} + (CH_3)_3Sn\cdot = (CH_3)_3Sn{:}^- \tag{41}$$

$$e^-_{am} + MnO_4^- = MnO_4^{2-} \tag{42}$$

When bond rupture accompanies electron addition, either an anion and a radical or an "anion-radical" forms:

$$e^-_{am} + (C_2H_5)_3SnBr = (C_2H_5)_3Sn\cdot + Br^- \tag{43}$$

Usually the radical undergoes dimerization, as in the following examples:

$$e^-_{am} + NH_4^+ = NH_3 + {}^1/_2\,H_2 \tag{44}$$

$$e^-_{am} + AsH_3 = AsH_2^- + {}^1/_2\,H_2 \tag{45}$$

$$e^-_{am} + RC{\equiv}CH = RC{\equiv}C{:}^- + {}^1/_2\,H_2 \tag{46}$$

$$e^-_{am} + R_2S = RS^- + {}^1/_2\,R{-}R \tag{47}$$

When the addition of two electrons causes bond rupture, either two anions or a "dianion" forms:

$$2\,e^{-}_{am} + Ge_2H_6 = 2\,GeH_3^{-} \tag{48}$$

$$2\,e^{-}_{am} + C_6H_5NHNH_2 = C_6H_5NH^{-} + NH_2^{-} \tag{49}$$

$$2\,e^{-}_{am} + C_6H_5{-}N{=}O = C_6H_5{-}N^{-}{-}O^{-} \tag{50}$$

Usually one or both of the anions undergoes ammonolysis, as in the following examples:

$$2\,e^{-}_{am} + N_2O + NH_3 = N_2 + OH^{-} + NH_2^{-} \tag{51}$$

$$2\,e^{-}_{am} + NCO^{-} + NH_3 = CN^{-} + OH^{-} + NH_2^{-} \tag{52}$$

$$2\,e^{-}_{am} + C_2H_5Br + NH_3 = Br^{-} + C_2H_6 + NH_2^{-} \tag{53}$$

$$2\,e^{-}_{am} + RCH{=}CH_2 + 2\,NH_3 = RCH_2CH_3 + 2\,NH_2^{-} \tag{54}$$

XI. Conclusions

We have observed that the physical properties of metal–ammonia solutions are consistent with the following qualitative descriptions of the solutions.

1. Extremely dilute solutions. Here the metal ions and electrons are essentially independent. The electrons occupy cavities around which the ammonia molecules are oriented with their protons nearest the cavities.

2. Moderately concentrated solutions. Here ammoniated metal ions are bound together by electrons into clusters such as M_2, M_3, etc.

3. Metallic solutions. The ammoniated metal ions are bound together by electrons much as ordinary metal ions of the same size would be in a molten metal.

In discussing the various physical properties of metal–ammonia solutions, we have stressed the quantitative aspects where possible; energetics have been particularly emphasized. It remains to be seen whether the energies which have been associated with various processes are self-consistent and fit into our picture of metal–ammonia solutions.

In Figure 11, we have plotted the energy of an electron against the logarithm of the metal concentration. We shall take the energy of a stationary electron *in vacuo* as zero. The bottom curve corresponds to the energy of a bound electron and the middle curve corresponds to the energy of a conduction electron with no kinetic energy. Transition *A* corresponds to the absorption of light of wavelength 15,000 A. (Section VIII-A). Transition *B* corresponds to the ammonation of a gaseous electron (Section VII-A). Transition *C* corresponds to the outer photoelectric process (Section VIII-C). Transition *D* corresponds both to the thermal excitation of a bound electron to the conduction level (Section VI-F) and the as yet unobserved photoexcitation to the conduction level (Section VIII-A). It will be noted that the energy of the bound electron decreases only slightly with increasing concentration. This is in agreement with the heat of dilution (Section VII-A) and the variation of the photoelectric limit with concentration (Section VIII-C). The energy of the conduction electron decreases with increasing concentration; in the saturated solution the energy is approximately equal to that of the bound electron (Section VI-F). It will be noted that Figure 11 has been constructed such that the various transition energies are at least in semiquantitative agreement with experiment.

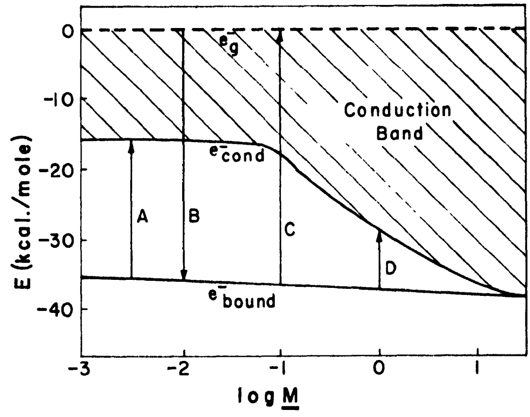


Fig. 11. Energy of electron in metal–ammonia solutions.

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Isocyanide Complexes of Metals

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I. General Survey of Isocyanides and Their Coordination Compounds

A. PREPARATION AND PROPERTIES OF ISOCYANIDES

Alkyl and aryl isocyanides, often called also isonitriles and carbylamines, can be considered to be derived from the tautomeric form of hydrocyanic acid, the hypothetic "isohydrocyanic acid," $|C{=}\overline{N}{-}H$.

Alkyl isocyanides are prepared by reaction of some metal cyanides with alkylating reagents, usually alkyl iodides. In this reaction the cyanides of alkalies or alkaline earths give mainly the alkyl cyanides, and only traces of isocyanides, while the cyanides of the transition metals give a mixture of cyanides and isocyanides, the ratio of the two isomers varying with the metal and the experimental conditions. The largest yields of alkyl isocyanides are obtained with silver and copper cyanides (21,24), silver cyanide being used almost without exception for preparative purposes.

Aryl isocyanides are usually prepared from aryl amines or aryl hydrazines with chloroform and alkali hydroxides, by the original Hofmann method or improvements of it (56,64). This method can also be used for the preparation of alkyl isocyanides, except for the lowest members, but in general it does not offer any advantage in comparison with the other.

Alkyl isocyanides are colorless liquids, somewhat more volatile than the corresponding cyanides; the difference in the boiling points of the lowest members of the two isomeric series is about 20°. They have penetrating and disgusting odors. They are extremely toxic, probably because of their ability to combine with hemoglobin (6,60, 102,114), and very unpleasant to handle. Alkyl isocyanides are highly reactive; they give polymers readily, and at high temperature (above 250°) rearrange to cyanides, the rearrangement being always accompanied by some polymerization.

Anhydrous acids cause alkyl isocyanides to polymerize, while aqueous acids hydrolyze them to an amine and formic acid (22):

$$RNC + HCl + 2\,H_2O \longrightarrow RNH_2{\cdot}HCl + HCOOH$$

TABLE I

Isocyanides[a]

Name	Formula	M.p., °C.	B.p., °C.	Density$^{\circ C.}$	Other data[b]
Methyl isocyanide	CH_3NC	−45	59.6/760 mm.	0.7557^{4}	(1) −26.7 (2) 318.7
Ethyl isocyanide	C_2H_5NC		78.1/760 mm.	0.7591^{4} 0.71498^{41}	(1) −23.8 (2) 479.2
Allyl isocyanide	C_3H_5NC		98/760 mm.	0.797^{17}	(3) 608.8
n-Propyl isocyanide	C_3H_7NC		99.5/760 mm.		(2) 638.9
Isopropyl isocyanide	C_3H_7NC		87/760 mm.	0.7596^{0}	
n-Butyl isocyanide	C_4H_9NC		116/760 mm.		
tert-Butyl isocyanide	$(CH_3)_3CNC$		91/37 mm.		
Isobutyl isocyanide	$(CH_3)_2C_2H_3NC$		114–7/760 mm.	0.7873^{4}	(2) 795.0
n-Amyl isocyanide	$C_5H_{11}NC$		50/45 mm.; 130/760 mm.		
Isoamyl isocyanide	$(CH_3)_2C_3H_5NC$		137/760 mm.		(2) 948.15
2-Methylbutyl isocyanide	$C_3H_8CHCH_2NC$		137.5/760 mm.		
Phenyl isocyanide	C_6H_5NC		64/20 mm., 165/760 mm.	0.977^{15}	
p-Tolyl isocyanide	$CH_3C_6H_4NC$		75/16 mm.; 183/753 mm.		
Benzyl isocyanide	$C_6H_5CH_2NC$		93/55 mm.; 198/760 mm.		(2) 1045.35
Pentamethylphenyl isocyanide	$(CH_3)_5C_6NC$	127–8			

[a] The data of this table are taken from Beilstein's *Handbuch der Organischen Chemie.*

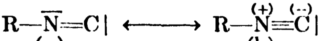
[b] (1) Molar heat of formation, kcal./mole. (2) Molar heat of combustion at constant pressure, kcal./mole. (3) Molar heat of combustion at constant volume, kcal./mole.

They are stable to alkalies under mild conditions, except the first member which undergoes a slow hydrolysis.

Aryl isocyanides are liquids or solids, colorless when pure, but usually of a green-yellow color because of slight polymerization. They, too, are more volatile than the corresponding cyanides; they cannot be distilled at atmospheric pressure without partial decomposition and rearrangement to cyanides. Phenyl isocyanide is liquid at room temperature and, among the most common members, is the least stable and the one with the most repulsive odor; *p*-tolyl isocyanide and *p*-anisyl isocyanide are solids and have less intense odors.

B. THE STRUCTURE OF ISOCYANIDES

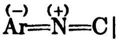
Isocyanides are among the very few substances with a lone electron pair on a carbon atom. Their structure can be considered as a hybrid of the two resonance forms (a) and (b)



$$\underset{(a)}{R-\overline{N}=C|} \longleftrightarrow \underset{(b)}{R-\overset{(+)}{N}\equiv\overset{(-)}{C}|}$$

The structure (a) should correspond to a bent molecule, and the structure (b) to a linear molecule; the resonance between the two forms would be possible only with a linear or nearly linear arrangement of the C–N–R bonds. Actually Powell found a value of 7 degrees for the angle C–N–CH_3 in the tetrakis(methylisocyano)iron(II) chloride (99), while the observation that the *p*-diisocyanobenzene shows no dipole moment (94) suggests that the isocyanide groups form an angle of 180 degrees with the rest of the molecule.

On the other hand, the possibility of a real difference in structure between alkyl and aryl isocyanides cannot be dismissed because, for the latter, another resonance form,



$$\overset{(-)}{Ar}=\overset{(+)}{N}=C|$$

which also leads to a linear structure, has to be taken into consideration.

C. "ADDITION COMPOUNDS" OF ISOCYANIDES

The presence of the lone electron pair on the carbon atom enables isocyanides to act as ligands in coordination compounds. Several addition compounds of isocyanides were already known long before the modern theory on the coordinate bond had been developed, and even before Werner's general theory on coordination. The organic chemists first came across these addition compounds while studying the synthesis of alkyl isocyanides; in fact, the product of the reaction between silver cyanide and alkylating reagents is an adduct of the type RNC·AgCN. In a similar way the esters of "ferrocyanic acid," which later on were recognized to be addition products of iron(II) and alkyl isocyanides, were at first investigated by the organic chemists and considered to be the trialkyl derivatives of the tricyanogen $(R_3C_3N_3)_3Fe$.

It was not unnatural that the acknowledged tendency of alkyl isocyanides to give addition compounds with silver, copper, and iron salts, led the chemists of that time to extend the research to most of the other metals, and from alkyl to aryl isocyanides. Before 1947, the addition compounds between isocyanides and the following metals were known: Cr^{III}, Fe^{II}, Fe^{III}, Co^{III}, Cu^{I}, Zn^{II}, Mo^{IV}, Ag^{I}, Cd^{II}, Pt^{II}, W^{IV}, and Hg^{II}. Some of these compounds, e.g., the derivatives of Fe^{II} and Pt^{II}, had some interest because of their remarkable stability and their occurrence in stereoisomeric forms, but on the whole they did not show any properties which suggested that isocyanides could play a role essentially different from the other known ligands.

D. TYPE OF BONDING IN THE ISOCYANIDE METAL COMPOUNDS

It was the recent developments of the theory of the chemical bond in coordination compounds that led chemists to look for new isocyano compounds, different from the conventional type already known. These views, first outlined by Pauling (97) and then developed and extended by other authors (8,9,16,59,95), are now, in their essential features, nearly universally accepted. Their main point consists in having realized that ligands can be divided into two limiting classes, according to the nature and electronic structure of the donor atom, and that the mechanism of coordination is essentially different for the two classes.

The ligands of the first class have donor atoms usually of high electronegativity, with a lone electron pair in the ultimate shell and no vacant orbitals on the same shell. They form "simple coordinate bonds" ("dative" σ-bonds) to nearly all the metal ions. The bonds formed by these ligands always have considerable ionic character, so that it had been possible to outline a theory considering them of a sheer ionic or ion-dipole type. For a given ligand, the stability of the bond increases with the ionic potential, that is, with the charge/radius ratio of the metal atom.

In general, the bonds formed to metal ions having inert gas electronic structures are of the ionic or partially ionic type; those to the transition metal ions are of the covalent type and may involve either only orbitals of the ultimate shell of the central atom (outer complexes) or also some of the orbitals of the penultimate shell (inner complexes). The nitrogen atom of ammonia and amines, the oxygen atom of the hydroxide ion, alcohols, ethers, ketones, etc., and the fluoride and chloride ions are typical donors of this class.

The ligands of the second class have donor atoms of usually low electronegativity, with a lone electron pair and vacant orbitals in the ultimate shell. They coordinate preferably or exclusively to the transition metals, their ions and the ions with 18 external electrons. In this respect ions such as Sc^{3+}, Ti^{4+}, and V^{5+}, which have 8 external electrons, are not to be considered of the transition type. The coordinate bonds formed by these ligands are always of the covalent type, with some double bond character,* and their complexes are of the "inner" type. The compounds of "divalent" carbon, namely, carbon monoxide, isocyanides, and cyanide ion, as well as nitrogen oxide and phosphorus trifluoride, which coordinate exclusively to transition metals, are the most typical representatives of this class. Other ligands, such as the esters of phosphorous acid, phosphines, arsines, stibines, thioalcohols, thioethers, and iodide ion, though essentially belonging to this class, form bonds with less double bond character.

As a consequence of this theory, the derivatives of CO, NO^+, CN^- (44), and RNC are comparable, and isocyanides are expected to form compounds of the same type as, or at least similar to, the metal carbonyls. The research which followed led in fact to the preparation of compounds of the predicted type.

It may be useful to consider briefly why it was predicted that compounds of this type would have the central atom in a low oxidation state. The double coordinate bond requires back-donation of *d* electrons of the central atom to the vacant orbitals of the donor in addition to donation of the lone electron pair from the ligand to the central atom.

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* For a discussion on this subject see the recent paper of Chatt (10).

This back-donation is usually only partial. Unfortunately, no accurate means are yet available to calculate or to measure the exact amount of double bonding in the coordinative bond, and even the values of the atomic electronegativities are only approximately known and not universally accepted. It is, however, possible to assert, at least in a qualitative way, that the net negative charge transferred from the donor to the acceptor is lessened when the coordinative bond has some double bond character, up to the point that it becomes practically nought when, as in the metal carbonyls, the amount of double bonding is very high. Therefore, according to Pauling's electroneutrality principle, the coordination compounds of this class are particularly stable when the central atom is in a low-valent state. For the transition metal it may be that oxidation states usually considered unstable for an element, and that do not occur in its "free" ions in aqueous solution, become stable. In some cases compounds in which the central atom has a zero or even a negative oxidation state can be obtained.

E. GENERAL FEATURES OF TYPICAL ISOCYANIDE COMPOUNDS

On the basis of these considerations, study of the coordination compounds of isocyanides has been undertaken from a new point of view since 1947. By that time, many partially substituted carbonyl derivatives (with ammonia, pyridine, phenanthroline, triphenylphosphine) were already known; but, as Blanchard (3) had remarked a few years before, there were no completely substituted carbonyl-type compounds. The above-recorded structural analogies between carbon monoxide and isocyanides led Hieber (39,40), and independently Klages and Mönkemeyer (61,62), to try the substitution reactions of $Ni(CO)_4$ with isocyanides, and thus the first isocyanide derivatives of a zero valent metal were obtained. A little later the same products were prepared from nickel(II) salts (67), that is, without use of $Ni(CO)_4$ as an intermediate. Afterwards, Malatesta and co-workers prepared the zero valent derivatives of the group VIA elements: $Cr(CNR)_6$ (68,69), $Mo(CNR)_6$ (70), and $W(CNR)_6$ (76); the nitrosylisocyano derivatives of iron and cobalt: $Fe(NO)_2(CNR)_2$ and $Co(NO)(CNR)_3$ (71,73); and the coordinately unsaturated zerovalent derivatives of palladium: $Pd(CNR)_2$ (79,81,84).

These results might appear to suggest a complete parallelism between carbon monoxide and isocyanides, but that is not exactly so.

In fact, it had already been pointed out by Hieber that the isocyanide molecule is far more polar than carbon monoxide. This difference results in a lower volatility of isocyanide derivatives with respect to carbonyls, and definite evidence for it is provided by comparison of the dipole moments of carbon monoxide and of alkyl and aryl isocyanides (26). The very low value of the dipole moment of carbon monoxide (0.12 D.) shows that the resonance structure $|\overset{(-)}{C}\equiv\overset{(+)}{O}|$ contributes to the actual structure of the molecule only in the measure required to neutralize the charge transfer between oxygen and carbon in the other and more important resonance form, $|C{=}O\rangle$ In the case of isocyanides, on the other hand, the most important resonance structure is the polar form, $R{-}\overset{(+)}{N}\equiv\overset{(-)}{C}|$ (26), which is not able to give a double coordinative bond, and it follows that the amount of double bond formed by isocyanides is less than that of carbon monoxide. Therefore isocyanides tend to stabilize low valent states, but to a smaller extent than carbon monoxide.

In fact, no isocyanide compounds are so far known corresponding to the carbonylmetallates $[Fe(CO)_4]^{2-}$, $[Co(CO)_4]^-$, and $[Rh(CO)_4]^-$, nor could stable zero valent complexes of the elements with odd atomic numbers like $[Co(CO)_4]_2$, $[Rh(CO)_4]_2$, and $[Mn(CO)_5]_2$ be obtained. The reaction between the dimeric cobalt carbonyl and isocyanides, which will be discussed later (Section V-B-1(b)), is indicative of this fact:

$$Co_2(CO)_8 + 5\,CNR \longrightarrow [Co(CNR)_5]^+[Co(CO)_4]^- + 4\,CO$$

This reaction shows that cobalt, in its isocyanide complexes, is stabilized in the +1 oxidation state. The same occurs with manganese, which forms the cation $[Mn(CNR)_6]^+$. In both cases the stabilization of the +1 oxidation state is so strong that these "univalent" derivatives are actually formed by "spontaneous" reduction of the divalent cobalt and manganese salts in presence of the ligand (that is, the solution itself acts as a reducing agent). They are indefinitely stable to air and can be obtained even as salts of strongly oxidizing anions.

For some metals, which, like iron and ruthenium, form very stable carbonyls, no isocyanide derivatives of an oxidation state lower than +2 have so far been obtained, although there are stable iron nitrosylisocyanide compounds of the type $Fe(NO)_2(CNR)_2$ (71,73), where the metal is assigned an oxidation number of −2. However, as the nitrosylcarbonyl metals do not show the dipole moments that might be expected if the NO molecules were present as positively charged groups (NO^+), the actual electronic distribution of nitrosyl compounds may not exactly correspond to the approximate pattern usually considered. In this case, the fact that there are no stable isocyanide substitution derivatives of compounds such as $[Fe(CO)_4]^{2-}$ may not be inconsistent with the stability of the iron nitrosylisocyanide compounds, formally considered as derivatives of Fe^{2-}.

F. ELEMENTS WHICH ARE KNOWN TO GIVE ISOCYANIDE COMPOUNDS

Isocyanide compounds of the following metals have been described:

IB	IIB	VIA	VIIA	VIII		
Cu	Zn	Cr	Mn	Fe	Co	Ni
Ag	Cd	Mo	—	Ru	Rh	Pd
Au	Hg	W	Re	—	—	Pt

The transition elements of groups VI, VII, and VIII generally form more than one type of isocyanide derivative, corresponding to different oxidation states. These compounds derive in most cases from metal atoms and ions with vacant *d* orbitals and are nearly always of the "inner" type. Their stability, as well as their properties and structure, varies greatly with the valence state of the central atom. Those with the metal in a very low oxidation state are the typical isocyanide complexes. The isocyanide derivatives of the elements of Groups IB and IIB are essentially different because they derive from metal ions with 18 outer electrons. In all compounds of these groups the metal displays the standard valence of its group, and the general features do not differ much from those of the complexes of usual ligands. For this reason, and because most of them were studied earlier, the compounds of the elements of groups IB and IIB will be dealt with first.

II. Isocyanide Compounds of the Elements of Groups IB and IIB

It is well known that the elements of the B groups do not form pure metal carbonyls, and that only those of Group IB give carbonyl hal-

TABLE II
Isocyanide Compounds of the Elements of Groups IB and IIB

Name	Formula[a]	Color and crystal form	M.p. or dec. temp., °C.	Other data	Ref.
	Isocyanide Compounds of Copper				
Iodomethylisocyanocopper(I)	$CuI(CNCH_3)$	White needles			36
Cyanoethylisocyanocopper(I)	$Cu(CN)(CNC_2H_5)$	Big colorless prisms			25
Cyano(*n*-propylisocyano)copper(I)	$Cu(CN)(CNC_3H_7)$	Big colorless rhombic plates			25
Cyano(isobutylisocyano)copper(I)	$Cu(CN)(CNC_4H_9)$	Big colorless rhombic prisms			25
Chloro(phenylisocyano)copper(I)	$CuCl(CNC_6H_5)$	White needles	184–5		63
Cyanobis(ethylisocyano)copper(I)	$Cu(CN)(CNC_2H_5)_2$				57
Chlorobis(phenylisocyano)copper(I)	$CuCl(CNC_6H_5)_2$	White needles	128		63
Cyanobis(phenylisocyano)copper(I)	$Cu(CN)(CNC_6H_5)_2$	White flakes	158–62		63
Cyanotris(ethylisocyano)copper(I)	$Cu(CN)(CNC_2H_5)_3$	Brown crystals			65
Cyanotris(*n*-amylisocyano)copper(I)	$Cu(CN)(CNC_5H_{11})_3$				65
Cyanotris(isoamylisocyano)copper(I)	$Cu(CN)(CNC_5H_{11})_3$				65
Chlorotris(phenylisocyano)copper(I)	$CuCl(CNC_6H_5)_3$	Colorless crystals	156		63
Cyanotris(phenylisocyano)copper(I)	$Cu(CN)(CNC_6H_5)_3$	White crystals	126–8		63, 65
Chlorotris(*p*-tolylisocyano)copper(I)	$CuCl(CNC_7H_7)_3$	Colorless crystals	170–2		63
Chlorotris(*p*-tolylisocyano)copper(I) with one mole ethanol	$[CuCl(CNC_7H_7)_3]\cdot C_2H_5OH$	Colorless prisms	170		63
Phenylacetylenide-tris(*p*-tolylisocyano)copper(I)	$Cu(CNC_7H_7)_3C_2C_6H_5$	White needles	100 (dec.)		63

Tetrakis(phenylisocyano)copper(I) chloride hexahydrate	$[Cu(CNC_6H_5)_4]Cl \cdot 6H_2O$	Colorless needles	102		63
Tetrakis(*p*-tolylisocyano)copper(I) chloride monohydrate	$[Cu(CNC_7H_7)_4]Cl \cdot H_2O$	Colorless crystals	127		63
Tetrakis(*p*-tolylisocyano)copper(I) perchlorate	$[Cu(CNC_7H_7)_4]ClO_4$	White needles	175		107
		Isocyanide Compounds of Silver			
Cyanomethylisocyanosilver(I)	$AgCN(CNCH_3)$	Colorless needles	75–6	$+7.0^b$	25
Cyanoethylisocyanosilver(I)	$AgCN(CNC_2H_5)$	Colorless needles	96–7	$+6.9^b$	25
Cyano(*n*-propylisocyano)silver(I)	$AgCN(CNC_3H_7)$	Colorless needles		$+6.7^b$	25
Cyano(isobutylisocyano)silver(I)	$AgCN(CNC_4H_9)$	Colorless needles		$+5.9^b$	25
Cyano(isoamylisocyano)silver(I)	$AgCN(CNC_5H_{11})$	Colorless needles		$+4.45^b$	25
Bis(*p*-tolylisocyano)silver(I) nitrate	$[Ag(CNC_7H_7)_2]NO_3$	White crystals	122–3		63
Tetrakis(*p*-tolylisocyano)silver(I) nitrate monohydrate	$[Ag(CNC_7H_7)_4]NO_3 \cdot H_2O$	White crystals	100–3		63
Tetrakis(*p*-tolylisocyano)silver(I) perchlorate	$[Ag(CNC_7H_7)_4]ClO_4$	White crystals	101		107
		Isocyanide Compounds of Gold			
Chlorophenylisocyanogold(I)	$AuCl(CNC_6H_5)$	White crystals			108
Chloro(*p*-tolylisocyano)gold(I)	$AuCl(CNC_7H_7)$	White crystals			108
Cyano(*p*-tolylisocyano)gold(I)	$Au(CN)(CNC_7H_7)$	White crystals	244 (dec.)		108
Chloro(*p*-anisylisocyano)gold(I)	$AuCl(CNC_7H_7O)$	White crystals			108
Tetrakis(phenylisocyano)gold(I) chloride	$[Au(CNC_6H_5)_4]Cl$	White crystals			108

(continued)

TABLE II (*continued*)

Name	Formula[a]	Color and crystal form	M.p. or dec. temp., °C.	Other data	Ref.
Tetrakis(*p*-tolylisocyano)gold(I) chloride	$[Au(CNC_7H_7)_4]Cl$	White crystals	190		108
Tetrakis(*p*-tolylisocyano)gold(I) tetraphenylborate	$[Au(CNC_7H_7)_4][Ph_4B]$	White crystals	175 (dec.)		108
Tetrakis(*p*-anisylisocyano)gold(I) chloride	$[Au(CNC_7H_7O)_4]Cl$	White needles			108
Trichloro(*p*-tolylisocyano)gold(III)	$AuCl_3(CNC_7H_7)$	Yellow crystals			108
Trichloro(*p*-anisylisocyano)gold(III)	$AuCl_3(CNC_7H_7O)$	Yellow crystals			108
Isocyanide Compounds of Zinc					
Dicyanobis(*n*-amylisocyano)zinc(II)	$Zn(CN)_2(CNC_5H_{11})_2$	Golden yellow powder			65
Dicyanobis(isoamylisocyano)zinc(II)	$Zn(CN)_2(CNC_5H_{11})_2$	Golden yellow powder			65
Dicyanobis(phenylisocyano)zinc(II)	$Zn(CN)_2(CNC_6H_5)_2$	Golden yellow crystals			65
Dicyanobis(benzylisocyano)zinc(II)	$Zn(CN)_2(CNC_7H_7)_2$	Golden yellow powder			65
Dichlorobis(*p*-tolylisocyano)zinc(II)	$ZnCl_2(CNC_7H_7)_2$	White crystals	146		107
Dibromobis(*p*-tolylisocyano)zinc(II)	$ZnBr_2(CNC_7H_7)_2$	White needles	166 (dec.)		107
Diiodobis(*p*-tolylisocyano)zinc(II)	$ZnI_2(CNC_7H_7)_2$	Pale yellow needles	155–60		107
Isocyanide Compounds of Cadmium					
Dichloro(*p*-tolylisocyano)cadmium(II)	$CdCl_2(CNC_7H_7)$	White crystals			108
Dibromo(*p*-tolylisocyano)cadmium(II)	$CdBr_2(CNC_7H_7)$				108

---

[a] Whenever the structure of the compound was not reported by the author, and cannot be unambiguously deduced from the text, the simplest name and formula have been adopted.

[b] Molar heats of formation from AgCN + RNC in kcal./mole.

ides. The tendency of these elements to form compounds with isocyanides is limited to Groups I and II. In Group IB the affinity toward isocyanides, generally strong, increases with the atomic number, while in Group IIB it is rather weak and varies irregularly, showing a maximum for cadmium and a minimum for mercury. If, however, the relative instability of mercury derivatives is ascribed to its tendency to be reduced to Hg_2^{2+}, then the same regularity as in Group IB can be observed.

In their isocyanide derivatives the metals of Groups IB and IIB have an electronic structure with 18 external electrons and display the usual oxidation state corresponding to their group. Only gold forms also rather unstable complexes in the trivalent state. Some of these isocyanide complexes were among the first to be prepared. Recently they have been reinvestigated, but on the whole the available experimental material is still rather incomplete and not organized in a satisfactory scheme.

A. COPPER

The alkylation of copper(I) cyanide with alkyl iodides was studied by Guillemard (1867) (25) and later by Hartley (36). The reaction is analogous to that of silver cyanide, but the yield of isocyanides is rather lower.

As in the case of silver, the reaction takes place in several stages (36). At a temperature not higher than 100°, and without solvent, the labile adduct $3CuCN{\cdot}CH_3I$ is formed, from which the methyl iodide can be recovered on heating. In presence of acetonitrile as solvent, or also—but not so neatly—without solvent at 135°, a stable compound is obtained, which can be crystallized from acetonitrile and has a composition corresponding to $CuCN{\cdot}CH_3I$. As this product gives off isocyanide on treating either with potassium cyanide or with silver sulfate, it is to be considered the iodomethylisocyanocopper(I),* $CuI(CNCH_3)$:

$$CuI(CNCH_3) + 3\,KCN \longrightarrow K_2Cu(CN)_3 + KI + CH_3NC$$

$$CuI(CNCH_3) + Ag_2SO_4 \longrightarrow AgI + Ag + CuSO_4 + CH_3NC$$

At higher temperature, the cyanomethylisocyanocopper is formed:

$$CuI(CNCH_3) + CuCN \longrightarrow CuCN(CNCH_3) + CuI$$

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* In the name of coordination compounds, the ligand RNC ought to be called "isocyanide" according to the proposed new rules of inorganic nomenclature. I apologize for having used the old shorter name "isocyano."

A not very stable compound containing two molecules of ethyl isocyanide, $CuCN(CNC_2H_5)_2$, was described by Hofmann and Bugge (57), who obtained it by reacting CuCN and C_2H_5NC in ether. Malatesta, in analogous experimental conditions, obtained instead (65) a number of compounds containing three molecules of isocyanide: $CuCN(CNR)_3$, where R is ethyl, *n*-amyl, isoamyl (optically active), or phenyl. A compound of the same type was prepared by Klages *et al.* (63) with *p*-tolyl isocyanide: $CuCN(CNC_7H_7)_3$. This compound, when dissolved and then reprecipitated from its solutions, loses a molecule of isocyanide and gives the more stable $CuCN(CN_7H_7)_2$, thus confirming Hofmann and Bugge's results. It may therefore be concluded that CuCN forms two series of complexes with two and three molecules of isocyanide, respectively, and that the compounds in which copper(I) is coordinatively saturated are the least

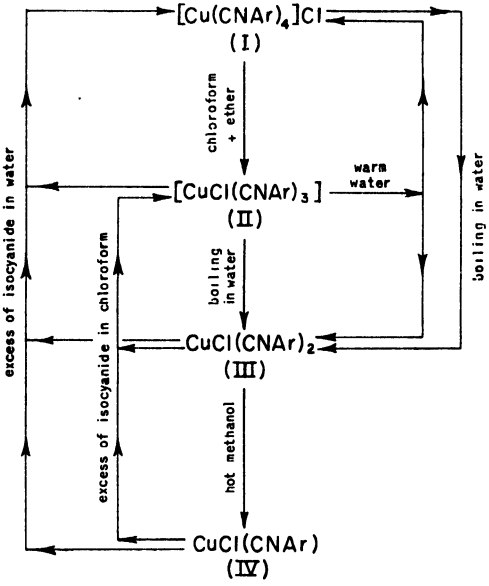


Fig. 1. Relationships among compounds of CuCl with phenyl and *p*-tolyl isocyanides. Direct preparations: I, from CuCl in aqueous ammonium hydroxide and excess CNAr in aqueous alcoholic solution; II, from a suspension of CuCl in ether with an excess of CNAr; III, from a suspension of CuCl in ether with two moles of CNAr; IV, from a suspension of CuCl in ether and one mole of CNAr.

stable and tend to transform into the others by loss of a molecule of ligand.

The compounds formed by CuCl with phenyl and *p*-tolyl isocyanide are very interesting (63). The relationships among the various products are summarized in Figure 1. Compounds I are formed by treating a solution of CuCl in aqueous ammonium hydroxide with an excess of isocyanide in alcohol. By careful dilution with water, the products separate in colorless crystals and can be recrystallized from water. They are uni-univalent electrolytes. On boiling in water, compounds I give off part of the isocyanide and are transformed into III. By dissolving in chloroform and reprecipitating with anhydrous ether, compounds I give II. These can also be obtained directly from CuCl and an excess of isocyanide in chloroform; from the chloroform solution the products separate by addition of anhydrous ether. Compounds II are nonelectrolytes. When treated with water, they rearrange to form compound I and III, the former remaining in solution and the latter separating as an oil that crystallizes on standing. Both compounds I and II give quantitatively III by boiling in water. Compounds III can also be prepared directly from CuCl and isocyanides, carrying out the reaction in chloroform with the required amount of ligand. On recrystallizing from hot methanol, compounds III give IV, which are also slowly formed by CuCl in ether and the calculated amount of isocyanide. Compounds IV are insoluble in all organic solvents. All these preparations and transformations are shown in Figure 1, together with some other obvious relationships among these compounds which are not mentioned in the text.

Copper(II) salts are immediately reduced by aryl isocyanides to copper(I) derivatives, while isocyanides transform into diarylurea and arylammonium chloride.

B. SILVER

Meyer (88) and Gautier (21,22), who first described the preparation of alkyl isocyanides by alkylation of silver cyanide, observed (1856) that compounds of the type AgCN·CNR are formed in the reaction between silver cyanide and alkyl iodides:

$$2\,\text{AgCN} + \text{RI} \longrightarrow \text{AgCN·CNR} + \text{AgI}$$

As was later shown by Hartley (1916) (34), this reaction proceeds in three stages. At room temperature, the adduct $(\text{AgCN})_2\cdot\text{CH}_3\text{I}$ is formed, which at 40° reacts with another molecule of methyl iodide to give $AgCN \cdot CH_3I$. This product, because of its decomposition by water into AgI and CH_3NC, is to be formulated as $AgI(CNCH_3)$, iodomethylisocyanosilver(I). At 100° the last stage of the alkylation reaction of AgCN takes place:

$$AgI(CNCH_3) + AgCN \longrightarrow AgI + AgCN(CNCH_3)$$

The same cyanoalkylisocyanosilver compounds are obtained (25) by reacting the corresponding isocyanide with silver cyanide in alcohol, and from potassium alkyl sulfate and potassium dicyanoargentate:

$$K[Ag(CN)_2] + ROSO_3K \longrightarrow AgCN(CNR) + K_2SO_4$$

In both cases the products are crystallized from hot alcohol.

The AgCN(CNR) compounds are colorless crystalline substances, with a rather high vapor pressure; on standing they first lose their transparency and then turn yellow. On heating they dissociate completely into silver cyanide and isocyanide. The dissociation of $AgCN(CNC_2H_5)$ begins at 60–70° and is complete at about 160°, but above 120° increasing amounts of ethyl cyanide are formed by rearrangement of the isocyanide. Below 120° the mixture contains about 96% of isocyanide, but the total yield is only 16%.

The derivatives of aryl isocyanides are rather unstable. An addition product of phenyl isocyanide and silver cyanide was prepared by A. W. Hofmann (1867) (55) and analyzed by K. A. Hofmann (1907) (57); it was assigned the formula $2\,AgCN \cdot (CNC_6H_5)$.

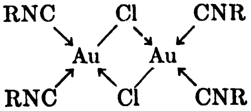
More interesting compounds have been recently prepared (1952) by Klages *et al.* (63). From *p*-tolyl isocyanide and a solution of silver nitrate in aqueous ammonium hydroxide at −20° a product is obtained which, recrystallized from alcohol as colorless needles, corresponds to $[Ag(CNC_7H_7)_4]NO_3 \cdot H_2O$. By addition of ether to a chloroform solution of this compound, the corresponding diisocyanide derivative is formed, viz., $[Ag(CNC_7H_7)_2]NO_3$. The perchlorate of tetrakis(*p*-tolylisocyano)silver $[Ag(CNC_7H_7)_4]ClO_4$ is analogous to the corresponding nitrate and is obtained at room temperature from an alcoholic solution (106).

C. GOLD

A number of aryl isocyanide derivatives of gold(I) and gold(III) have been recently (1956) prepared by Sacco and Freni (108). The derivatives of gold(III) were obtained by reacting a cold alcoholic solution of chloroauric(III) acid with aryl isocyanides (two moles per mole of $HAuCl_4$). They are yellow crystalline substances, sparingly soluble in organic solvents, of composition corresponding to $AuCl_3(CNR)$. Their molecular weights were not determined, but in consideration of the dimeric structure of $AuCl_3$ (18) they are likely to be monomeric. The trichloroarylisocyanogold(III) compounds are rather unstable and are spontaneously reduced to the derivatives of gold(I) in presence of an excess of the isocyanide itself. When the reduction was carried out by warming either the trivalent derivatives or the solution of chloroauric acid with a very large excess of the isocyanide in alcoholic solution, the univalent compounds of formula $[Au(CNR)_4]Cl$ were obtained. These are crystalline substances, stable in the solid state, but unstable in solution unless a large excess of isocyanide is present. The corresponding tetraphenylborate, obtained by exchange reaction with $Na[B(C_6H_5)_4]$ is, however, stable in solution and shows the character of a strong uni-univalent electrolyte. The cation $[Au(CNR)_4]^+$ is colorless, like the analogous copper and silver ions, and is one of the very few examples of coordinatively saturated gold(I).

The chlorides of tetrakis(arylisocyano)gold(I) can be recrystallized from hot alcohol only in presence of free isocyanide; otherwise they are transformed into the chlorobis(arylisocyano)gold(I) compounds, $AuCl(CNR)_2$. These were also obtained directly from the gold(III) derivatives, by boiling them in alcohol in presence of a moderate excess of isocyanide (equal weights of trivalent complex and isocyanide).

The chlorobis(arylisocyano)gold(I) compounds are yellow crystalline substances, soluble in most organic solvents, stable both in the solid state and in solution. Their molecular weights were not determined, but they are likely to be dimeric with a chlorobridged structure:



D. ZINC

Isocyanides have a very low affinity for zinc. Their tendency to coordinate to the zinc ion, Zn^{2+}, is lower than for the corresponding amines, and this fact suggested a new method (107) for the separation of the amine–isocyanide mixture which is always obtained in the preparation of isocyanides by the Hofmann method. By reacting ethyl iodide and zinc cyanide, Guillemard obtained (25) a small amount of isocyanide, but did not isolate any addition product.

Some addition compounds of zinc cyanide with alkyl and aryl isocyanides were prepared by Malatesta (1947) (65) by treating $Zn(CN)_2$ with a slight excess of isocyanide. They are colorless powders of formula $Zn(CN)_2(CNR)_2$, where R is *n*-amyl, isoamyl, (optically active), benzyl, or phenyl. The derivatives of alkyl isocyanides are water soluble and could not be obtained as crystals; the aromatic derivative is insoluble in water and was obtained in the crystalline state.

The zinc halogenide derivatives of *p*-tolyl isocyanide, $ZnX_2(CNC_7H_7)_2$ ($X = Cl, Br, I$), were prepared (107) by reacting a solution of isocyanide in ether with an ethereal solution of $ZnCl_2$, an aqueous alcohol solution of $ZnBr_2$, and an alcohol solution of ZnI_2 respectively.

E. CADMIUM

The reaction of cadmium cyanide and ethyl iodide was studied by Guillemard who observed the formation of ethyl isocyanide, but did not describe any addition product of it with the cadmium salt (25). Later, Hölzl studied the methylation of silver tetracyanocadmiate with methyl iodide and of sodium tetracyanocadmiate with dimethyl sulfate (53).

Dry and finely powered $Ag_2[Cd(CN)_4]$ was shaken for ten days with an excess of CH_3I in the dark at room temperature. The solid mass was extracted with hot methanol; on cooling the solution, a substance separated which, after drying in vacuum, had a composition corresponding to

$$Cd_4(CN)_4(OH)_4(CNCH_3)\cdot 4\,H_2O$$

(V)

As the presence of the hydroxy groups had to be ascribed to partial hydrolysis, the reaction was repeated excluding any trace of water as carefully as possible. The solid mass obtained under these conditions, recrystallized from water and dried in vacuum, gave white crystals of composition corresponding to

$$Cd_2(CN)_2(OH)_2(CNCH_3)$$

(VI)

By shaking for ten days a mixture of finely powdered $K_2[Cd(CN)_4]$ with a large excess of dimethyl sulfate, a liquid and a solid mass were obtained. The solid, extracted with hot anhydrous methanol, gave colorless, water-soluble crystals which analyzed as

$$Cd_3(CN)_5(OH)(CNCH_3)_2$$

(VII)

The aqueous solution of this compound reacted alkaline.

The liquid layer, after removal of the excess of dimethyl sulfate by distillation under reduced pressure, gave a solid residue which was recrystallized from hot methanol and shown to be a cadmium salt of methyl sulfuric acid, coordinated to isocyanide, possibly

$$Cd(CNCH_3)_4(CH_3SO_4)_2 \quad \text{or} \quad Cd(CNCH_3)_3(CH_3SO_4)_2$$

(VIIIA) (VIIIB)

The reaction between $K_2[Cd(CN)_4]$ and $(CH_3)_2SO_4$ in molar ratio 1:1, gave instead a product of the formula

$$Cd_6(CN)_{11}(OH)(CNCH_3)$$

(IX)

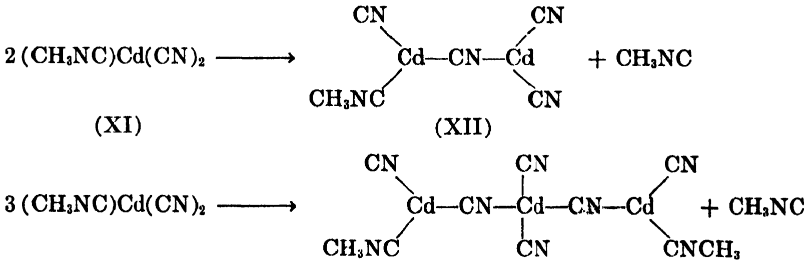
The results of this research were summarized and interpreted by Hölzl (53) as follows: the first product formed in the reaction between methyl iodide and silver tetracyanocadmiate is a hypothetical dicyanobis(methylisocyano)cadmium

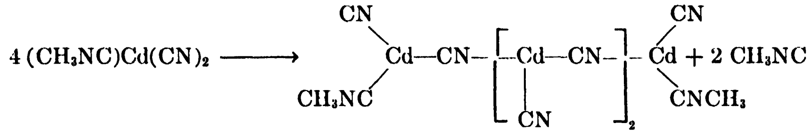
$$Cd(CN)_2(CNCH_3)_2$$

(X)

This is unstable and immediately gives off one molecule of isocyanide, thus forming a tricoordinate intermediate (XI) which condenses to polynuclear structures with further elimination of isocyanide.

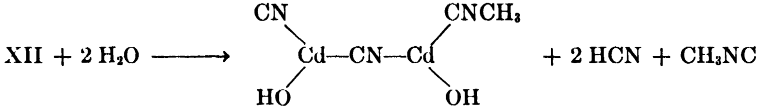
$$\underset{(X)}{(CH_3NC)_2Cd(CN)_2} \longrightarrow \underset{(XI)}{(CH_3NC)Cd(CN)_2} + CH_3NC$$



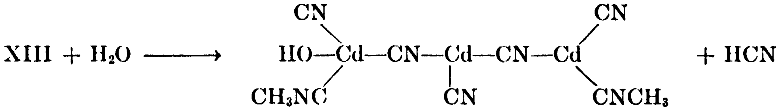


(XI) (XIV)

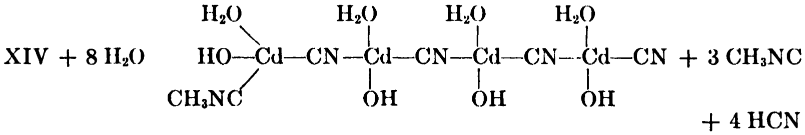
Compounds XII, XIII, and XIV are then hydrolyzed by water to compounds which correspond to VI, VIII, and V, respectively:



(VI)



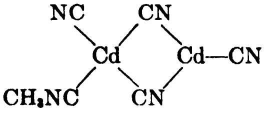
(VII)



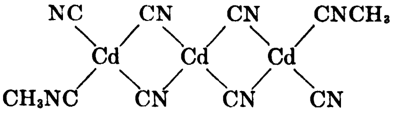
(V)

Hölzl thought that the μ-hydroxy forms, which could be postulated as well as the μ-cyano, were to be discarded because (*a*) the aqueous solutions of V and VI have alkaline reaction, as would be expected for compounds with terminal and not with bridging hydroxy groups; (*b*) compound VII, which cannot be formulated as a μ-hydroxy complex, would not fit in with the analogous compounds V and VI.

Hölzl was, however, uncertain whether to assign the cadmium atoms a coordination number of three or four; in fact, compounds XII and XIII could also be written as follows:



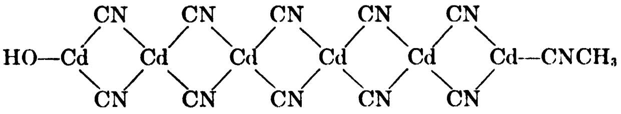
(XIIB)



(XIIIB)

Exception might be taken to Hölzl's conclusion that the alkaline nature of the compounds is indicative of CN bridges and terminal

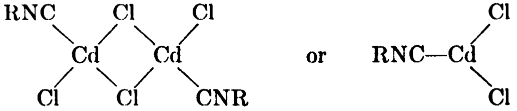
OH groups; the alkaline reaction could be due to hydrolysis or oxidation and hydrolysis of methyl isocyanide. It is my personal experience that, of all isocyanides, methyl isocyanide is the most readily converted into methylamine. Besides, the fact that compound XII does not tend to bind water, not even in diluted aqueous solution, would be better explained by a structure with double cyanide bridges, e.g.,



(VIIB)

Anyway, as these structures were assigned mostly on the basis of analytical evidence, which alone is not sufficient for compounds of such a complexity, both the identification of these substances and their formulation should not be considered completely reliable.

The dichloro- and dibromo(*p*-tolylisocyano)cadmium, $CdCl_2(CNC_7H_7)$ and $CdBr_2(CNC_7H_7)$, prepared by Sacco (108), are the only known compounds of cadmium with aryl isocyanides. They are colorless crystalline substances, and were obtained by reacting cadmium halides with an excess of *p*-tolyl isocyanide in alcohol. Their molecular weights are not known, and therefore it cannot be decided whether they are dimeric with tetracoordinate cadmium atoms, or monomeric and tricoordinate, viz.:



It may be noticed that, as in the case of methyl isocyanide, only one molecule of isocyanide is coordinated to the cadmium atom.

F. MERCURY

The reaction between mercuric cyanide, $Hg(CN)_2$, and ethyl iodide was first studied by Guillemard (25) who could not isolate any addition product of the mercuric salt with ethyl isocyanide. Negative results were obtained also by Calmels (7) and by Chwala (11), who affirmed that isocyanides reduce mercuric to mercurous salts, giving no addition products. Later Hartley (35) repeated the reaction between $Hg(CN_2)$ and ethyl iodide and observed a compound of composition corresponding to $HgI_2(CNC_2H_5)_2$. This product, which could also be obtained from HgI_2 and ethyl isocyanide, seemed to contain a dimeric derivative of the isocyanide itself.

Recently Klages *et al.* (63) succeeded in preparing the addition product between mercuric chloride and two moles of *p*-tolyl isocyanide. By treating an ethereal solution of *p*-tolyl isocyanide, cooled to −20°, with an ethereal solution of mercuric chloride, the compound $HgCl_2(CNC_7H_7)_2$ separated as colorless crystals, soluble in pyridine and slightly soluble in chloroform. On standing the compound decomposed with separation of Hg_2Cl_2.

When the reaction between isocyanide and $HgCl_2$ is carried out at higher temperature, and with an excess of isocyanide, the latter is oxidized according to the reactions:

$$4\,Hg^{2+} + 2\,ArNC + 3\,H_2O \longrightarrow 2\,Hg_2^{2+} + (Ar\text{—}NH)_2CO + CO_2 + 4\,H^+$$

$$4\,H^+ + 4\,ArNC + 4\,ROH \longrightarrow ArNH_3^+ + 4\,HCO_2R$$

III. Isocyanide Compounds of the Group VIA Elements

The elements of groups IA–VA do not show any tendency to form complexes with isocyanides. The capacity to coordinate isocyanides begins to manifest itself with the transition metals of Group VIA: chromium, molybdenum, and tungsten. The same trend is observed for carbonyl compounds. The known isocyanide derivatives of these elements can be divided into two main classes:

1. Compounds with the central atom in a comparatively high oxidation state (three and four). They are usually ill-defined and their stability increases with the atomic number of the central atom.

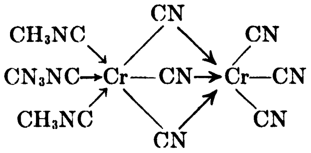
2. Compounds with the central atom in the oxidation state zero. They are well-defined and stable substances, with a carbonyl-like structure. The ease of formation of these compounds decreases very rapidly with increasing atomic number of the central atom, while the opposite occurs for the hexacarbonyls of the metal of this group, among which chromium hexacarbonyl is the most difficult to prepare. The chemical stability of these compounds, e.g., the resistance to oxidation, decreases, too, but very slowly, from chromium to tungsten. The same effect can be observed for the zero valent derivatives of the series Ni, Pd, and Pt (though Pt(0) compounds are not known), and it is probably due to the increase in electronegativity.

A. CHROMIUM

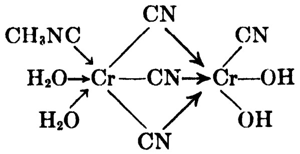
1. Derivatives of Chromium(III)

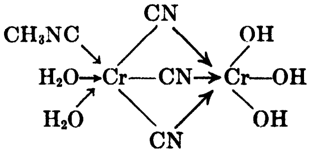
The affinity of chromium(III) for isocyanides is extremely poor, and the addition compounds between chromium(III) salts and isocyanides, if ever they form, are immediately decomposed by water.

Hölzl (51) studied the alkylation of $K_3[Cr(CN)_6]$ with dimethyl sulfate and of $Ag_3[Cr(CN)_6]$ with methyl iodide. In this way he could only obtain mixtures of polynuclear products, probably with bridging CN groups, containing some molecules of isocyanides. In Hölzl's opinion, the first product formed during the course of the reaction is a hypothetical "methylchromiumcyanide," that is, a tricyanotris(methylisocyano)chromium(III), which immediately loses hydrocyanic acid and methyl isocyanide to give a still hypothetical dinuclear compound:



By hydrolysis this gives the products which were actually observed in the reaction, and were written as:





The latter was also isolated as a dihydrate and a pentahydrate. These products are soluble in water and very difficult to crystallize; their identification is not completely satisfactory, and the formulas proposed by Hölzl do not seem sufficiently proved.

TABLE III
Isocyanide Compounds of the Group VIA Elements

Name	Formula	Color and crystal form	M.p. or dec. temp, °C.	Other data[a]	Ref.
	Isocyanide Compounds of Chromium				
Pentacarbonyl(*p*-anisylisocyano) chromium(0)	$Cr(CO)_5(CNC_7H_7O)$	Colorless needles	107–8		47
Hexakis(phenylisocyano)chromium(0)	$Cr(CNC_6H_5)_6$	Red crystals	178.5	(1) -327×10^{-6}	69
Hexakis(*p*-tolylisocyano)chromium(0)	$Cr(CNC_7H_7)_6$	Red crystals	152.8	(1) 228×10^{-6}	69
Hexakis(*p*-anisylisocyano)chromium(0)	$Cr(CNC_7H_7O)_6$	Red crystals	124.4	(1) -448×10^{-6}	69
Hexakis(*m*-chlorophenylisocyano)-chromium (0)	$Cr(CNC_6H_4Cl)_6$	Orange-red crystals	156		
Hexakis(*p*-chlorophenylisocyano)-chromium(0)	$Cr(CNC_6H_4Cl)_6$	Bright red crystals	~220(dec.)	(1) -101×10^{-6}	69
Hexakis(3-chloro-2-methylphenyl-isocyano)chromium(0)	$Cr(CNC_7H_6Cl)_6$	Red crystals	192.5	(1) -541×10^{-6}	69
Hexakis(4-chloro-2-methylphenyliso-cyano)chromium(0)	$Cr(CNC_7H_6Cl)_6$	Red crystals with golden reflectances	172		69
Hexakis(2,4-dimethylisocyano)-chromium(0)	$Cr(CNC_8H_9)_6$	Red crystals			69
Hexakis(2,5-dichlorophenylisocyano)-chromium(0)	$Cr(CNC_6H_3Cl_2)_6$	Red crystals with golden reflectances	166	(1) -127×10^{-6}	69

	Isocyanide Compounds of Molybdenum				
Pentacarbonyl(*p*-anisylisocyano)-molybdenum(0)	$Mo(CO)_5(CNC_7H_7O)$	Colorless crystals	105–6		47
Hexakis(phenylisocyano)molybdenum(0)	$Mo(CNC_6H_5)_6$	Red needles with green reflectances		(2) 207 × 10^{-6}	70
Hexakis(*p*-tolylisocyano)molybdenum(0)	$Mo(CNC_7H_7)_6$	Orange leaflets			70
Hexakis(*m*-chlorophenylisocyano)-molybdenum(0)	$Mo(CNC_6H_4Cl)_6$	Yellow-orange crystals			70
Hexakis(4-chloro-2-methylphenylisocyano)molybdenum(0)	$Mo(CNC_7H_6Cl)_6$	Yellow-orange crystals		(2) 156 × 10^{-6}	70
Hexakis(6-chloro-2-methylphenylisocyano)molybdenum(0)	$Mo(CNC_7H_6Cl)_6$	Brick-red crystals		(2) 115 × 10^{-6}	70
Hexakis(2,4-dichlorophenylisocyano-molybdenum(0)	$Mo(CNC_6H_3Cl_2)_6$	Yellow-orange crystals			70
	Isocyanide Compounds of Tungsten				
Pentacarbonyl(*p*-anisylisocyano)-tungsten(0)	$W(CO)_5(CNC_7H_7O)$	Colorless crystals	121.5		47
Hexakis(phenylisocyano)tungsten(0)	$W(CNC_6H_5)_6$	Dark red prisms	120–30	(2) 186 × 10^{-6}	76
Hexakis(*p*-chlorophenylisocyano)-tungsten(0)	$W(CNC_6H_4Cl)_6$	Red prisms with gold-green reflectances		(2) 240 × 10^{-6}	76
Hexakis(3-chloro-2-methylphenylisocyano)tungsten(0)	$W(CNC_7H_6Cl)_6$	Red prisms with green reflectances	205–7	(2) 203 × 10^{-6}	76

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[a] Magnetic susceptibility, χ_M, of the solid at (1) 18° and (2) 20°.

2. Derivatives of Chromium(0)

Chromium hexacarbonyl is an extremely stable substance which shows very little tendency to give substitution reactions, and no completely substituted derivatives can be obtained from it, not even under very drastic conditions. Actually, the only known substitution compound is the pentacarbonyl(*p*-anisylisocyano)chromium, $Cr(CO)_5(CNC_7H_7O)$, prepared by reacting $Cr(CO)_6$ and *p*-anisyl isocyanide (47) in a sealed tube at 120–130°. This behavior agrees with the observation of Hieber and co-workers (47) that the tendency of metal carbonyls to give substitution reactions decreases rapidly in the sequence $Ni > Co > Fe > Cr$. Hexarylisocyanochromium compounds, $Cr(CNAr)_6$, formally derived from chromium carbonyl, were, however, obtained in a different way by Malatesta and co-workers (68,69). When an alcoholic suspension of chromium(II) acetate is treated with an excess of aryl isocyanide, a lively reaction occurs, which has to be considered a disproportionation of chromium(II) to chromium(III) and chromium(0), and may be written as follows:

$$3\,Cr^{2+} + 18\,RNC \longrightarrow Cr(CNR)_6 + 2\,[Cr(CNR)_6]^{3+}$$

The hexarylisocyanochromium(III) salts could not be isolated, but the yield of $Cr(CNR)_6$ agrees with the above equation. Thus, by reacting 3 moles of $Cr(CH_3COO)_2$ with 6 moles of C_6H_5NC, 0.309 mole of $Cr(CNC_6H_5)_6$ was obtained and 1.77 moles of $Cr(CH_3COO)_2$ remained in the solution. The same reaction, repeated with 3 moles of chromium(II) acetate and 18 moles of isocyanide, gave 0.945 mole of $Cr(CNC_6H_5)_6$.

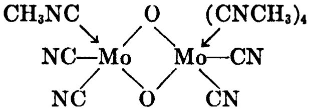
Hexarylisocyanochromium compounds are diamagnetic, crystalline substances, of colors varying from yellow to red with green or metallic reflectances. They are quite stable to air and melt without decomposition in a rather high temperature range (125–200°). They are soluble in chloroform and benzene, sparingly soluble in alcohol, insoluble in water. The solutions are stable to air in the cold, but decompose on prolonged boiling. Hexarylisocyanochromium compounds are slowly decomposed by aqueous solutions of strong mineral acids, but are not affected by alkali, not even by hot sodium alcoholate.

B. MOLYBDENUM

1. Derivatives of Molybdenum(IV)

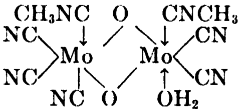
These compounds were described by Hölzl and Xenakis (50) in their work on the alkylation of the octacyanomolybdates (1927).

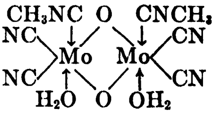
Silver octacyanomolybdate was reacted with methyl iodide at a mild temperature. The reaction mixture was extracted with anhydrous methanol, giving a solid residue and a solution from which a yellow crystalline substance (XV) separated. This product was very hygroscopic and had an isocyanide smell. It had an analysis corresponding to $(CH_3)_4Mo(CN)_8$ and was formulated as $Mo(CN_4)(CNCH_3)_4$, that is as a "methylmolybdocyanide," tetracyanotetrakis(methylisocyano)molybdenum(IV). The solid residue was further extracted with water; the aqueous solution gave on concentration a second compound (XVI), probably derived from XV by hydrolysis:



(XVI)

Finally the water-insoluble residue, treated with dilute hydrochloric acid, gave a yellow solution from which other hydrolysis products were isolated, e.g.:





Other compounds, such as $H_4[Mo(CN)_4(OH)_4] \cdot 3\,CNCH_3$, were considered addition compounds of the tetrahydroxotetracyanomolybdic(IV) acid and not true isocyanide coordination compounds.

When the methylation was carried out with $K_4[Mo(CN)_8]$ and $(CH_3)_2SO_4$, and the reaction mixture washed with water to remove CH_3SO_4K, a compound $[Mo(CN)_4(H_2O)_2(CNCH_3)_2] \cdot 4\,H_2O$, was obtained, which was considered a hydrolysis product of XV.

It may be observed that all these substances, though better defined than the analogous chromium(III) derivatives described by the same authors, are all rather unstable and readily hydrolyzed. These facts show that the affinity of isocyanides for Mo^{IV} is still very poor.

2. *Derivatives of Molybdenum(0)*

Pentacarbonyl(*p*-anisylisocyano)molybdenum, $Mo(CO)_5(CNC_7H_7O)$ was prepared by Hieber (47) on heating a mixture of $Mo(CO)_6$ and *p*-anisyl isocyanide in a sealed tube, and is strictly similar to the analogous compound of chromium. No further substituted products could be obtained by this way.

Like chromium, molybdenum forms hexakis(arylisocyano) compounds (70) which can be considered formally as the products of total substitution of the hexacarbonyl, although they cannot be prepared from it. For the preparation of the hexakis(arylisocyano)molybdenum a reaction similar to that described for chromium was not possible, and one of the following methods, all giving rather poor yields, had to be adopted:

1. Reduction of an alcoholic suspension of MoO_3 with hydrazine hydroxide, in presence of an aryl isocyanide.

2. Reduction of a solution of $Mo_2O_3(S_2COC_2H_5)_4$ (ethylxanthate) in methylene chloride, with hydrazine hydroxide in presence of an aryl isocyanide.

3. Reduction of MoO_3 to $MoCl_3$, in hydrochloric acid with magnesium powder, followed by addition of alcohol, hydrazine acetate, and an aryl isocyanide.

4. Reduction of a mixture of $MoCl_6$, isocyanide, and magnesium powder suspended in alcohol, by dropwise addition of glacial acetic acid. This method gave the best results. The crude products were then dissolved in methylene chloride and quickly reprecipitated by addition of anhydrous alcohol.

The hexakis(arylisocyano)molybdenum compounds were thus obtained as crystalline red powders, with golden or green reflectances, soluble in methylene chloride, chloroform, and benzene, insoluble in alcohol. They are indefinitely stable in vacuum, while in presence of air they alter within a few days; the decomposition is much more rapid in solution. Some of these compounds show a slight paramagnetism which is probably due to some impurities.

C. TUNGSTEN

1. Derivatives of Tungsten(IV)

The derivatives of tungsten(IV) were prepared by Hölzl and Zymaris (1929) by alkylation of silver octacyanotungstates(IV) with methyl iodide (52). The various products obtained by this reaction are shown by analysis to contain tungsten, cyano groups, methyl groups, and water, and it would have been possible, by analogy with the other elements of this group, to formulate them as hydrolysis products of a "methylcyanotungstate" (tetracyanotetrakis(methylisocyano)tungstate(IV)), which can be assumed to be the primary product in the alkylation reaction:

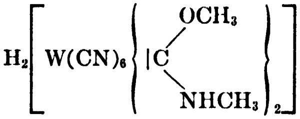
$$Ag_4[W(CN)_8] + 4\,CH_3I \longrightarrow (CH_3)_4W(CN)_8 + 4\,AgI$$

However, in order to explain why all these compounds have strong acid reaction in aqueous solution, and why both water and isocyanide are fairly strongly bound, Hölzl assumed them to be derivatives of $H_4[Mo(CN)_8]$, containing as ligand a product of primary hydrolysis and esterification of the isocyanide $CH_3O—\bar{C}—NHCH_3$.

Thus a substance analyzing as $C_8H_{16}O_2N_8W$ (XVII), which could have been written:

$$[W(CN)_4(CNCH_3)_4](H_2O)_2$$

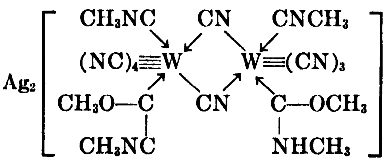
was formulated by Hölzl as:



Similarly, the product obtained from XVII and $AgNO_3$, which analyzed as $C_{10}H_{10}ON_7WAg$, and could have been written:

$$Ag[W(CN)_4(OH)(CNCH_3)_3]$$

was instead formulated as:



and so forth.

In Hölzl's opinion this peculiar behavior of tungsten is due to the fact that the starting material, the silver octacyanotungstate, is actually a hydrogen silver salt of composition between $Ag_3H[W(CN)_8]$ and $Ag_2H_2[W(CN)_8]$. Because of the acidity of the medium, the isocyanide formed by alkylation takes up a molecule of water or alcohol and gives an intermediate hydrolysis product, not stable in the free state but stable as ligand. All this is quite possible, but in my opinion not sufficiently proved, and the suggestion that some of these compounds are derivatives of W^V seems even less supported.

In any event, Hölzl's research shows that the alkylation derivatives of $H_4[W(CN)_8]$ are undoubtedly more stable then those of $H_3[Cr(CN)_6]$ and $H_4[Mo(CN)_8]$, and that it is possible to isolate a compound of composition very near to that of the hypothetical product of primary esterification, $W(CN)_4(CNCH_3)_4$, as well as hydrolysis and condensation derivatives in which the isocyanide molecules are fairly strongly bound.

2. Derivatives of Tungsten(0)

Like chromium and molybdenum carbonyls, tungsten hexacarbonyl reacts under drastic conditions with *p*-anisyl isocyanide to give the monosubstituted pentacarbonyl(*p*-anisylisocyano)tungsten, $W(CO)_5(CNC_7H_7O)$ (47).

The hexakis(arylisocyano) tungsten compounds, $W(CNR)_6$, were also obtained (76), but their preparation proved very difficult and was successful only with a few aryl isocyanides, namely, phenyl, *p*-chlorophenyl, and 2-methyl-4-chlorophenyl isocyanide. The preparation was carried out by slow addition of tungsten(VI) chloride to a mixture of isocyanide, magnesium powder, anhydrous alcohol, and a few drops of glacial acetic acid. During the addition the mixture was stirred vigorously and cooled to below 0°. The precipitate thus obtained was washed thoroughly with alcohol, dissolved in benzene, and chromatographed through an alumina column. On diluting the eluted solution with anhydrous alcohol, the product separated in a pure state. Yields are about 10%.

The hexakis(arylisocyano)tungsten(0) compounds are diamagnetic crystalline substances, with red colors and green-golden reflectances. They are soluble in chloroform, methylene chloride, benzene, acetone and pyridine, insoluble in alcohol and ether. They are stable to air for a few hours.

IV. Isocyanide Compounds of the Group VIIA Elements

A comparison between the isocyanide derivatives of manganese and rhenium is hardly possible, for the latter have scarcely been investigated, and only compounds of totally different types are known for the two elements. Of manganese, a number of salts of the cations $[Mn(CNR)_6]^{2+}$ and $[Mn(CNR)_6]^+$ have been prepared, while of rhenium the only isocyanide derivative described so far is a substitution product of $ReCl(CO)_5$. Anyway, it looks as if rhenium would not give isocyanide compounds as stable as those of manganese.

A. MANGANESE

Manganese(II) salts, as well as the coordination compounds of Mn^{II} and Mn^{III}, do not show any tendency to react with isocyanides under the most varied conditions. This is probably the reason why no isocyanide derivatives of manganese were known until a few years ago.

1. Derivatives of Manganese(I)

Sacco observed (109) that the anhydrous manganese(II) iodide behaves in a way different from the other manganous salts. In alcoholic solution it reacts with alkyl and aryl isocyanides according to the equation:

$$2\,MnI_2 + 12\,CNR \longrightarrow [Mn(CNR)_6]I + [Mn(CNR)_6]I_3$$

This reaction is not a disproportionation of the type $Mn^{II} \rightarrow Mn^{I} + Mn^{III}$, as it might appear at first, because the compound $[Mn(CNR)_6]I_3$ is not a derivative of manganese(III) but a triodide of hexaisocyanomanganese(I). This formulation agrees with the following facts: (*1*) the compound $[Mn(CNR)_6]I_3$ is diamagnetic, while a hexacoordinated cation of Mn^{III} would be expected to be paramagnetic; (*2*) in nitrobenzene solution, its electrical conductivity has the standard value of a strong uni-univalent electrolyte; and (*3*) it can be reduced to the corresponding iodide under the same mild conditions required for the reduction of iodine to iodide ion (e.g., with thiosulfate). On the other hand, the oxidation of $[Mn(CNR)_6]^+$ with strong oxidizing agents leads to the corresponding Mn(II) compound, but on no account can the trivalent derivatives be obtained.

The separation of the iodide and triiodide from the reaction mixture is usually easy because of their different solubilities in alcohol, the iodide being far the more soluble.

In the case of methyl isocyanide, however, the iodide is so soluble that it would be very difficult to obtain it in a pure state from the original alcoholic solution. The hexakis(methylisocyano)manganese(I) iodide was best prepared in the following way: by addition of iodine to the reaction mixture, all the iodide was converted into the

TABLE IV
Isocyanide Compounds of Manganese

Name	Formula	Color and crystal form	M.p. or dec. temp., °C.	Other data[a]	Ref.
Hexakis(methylisocyano)-manganese(I) iodide	$[Mn(CNCH_3)_6]I$	White needles	263–64		110
Hexakis(methylisocyano) manganese(I) triodide	$[Mn(CNCH_3)_6]I_3$	Light blue crystals	151–52		112
Hexakis(methylisocyano)-manganese(I) perchlorate	$[Mn(CNCH_3)_6]ClO_4$	White crystals	161 (dec.)		112
Hexakis(methylisocyano)-manganese(I) tetraphenylborate	$[Mn(CNCH_3)_6][B(C_6H_5)_4]$	White needles	250–1		112
Hexakis(ethylisocyano)manganese(I) iodide	$[Mn(CNC_2H_5)_6]I$	White needles	188–90		112
Hexakis(ethylisocyano)manganese(I) triodide	$[Mn(CNC_2H_5)_6]I_3$	Brown needles	272		112
Hexakis(ethylisocyano)manganese(I) tetraphenylborate	$[Mn(CNC_2H_5)_6][B(C_6H_5)_4]$	White needles	134–5		112
Hexakis(cyclohexylisocyano)-manganese(I) iodide	$[Mn(CNC_6H_{11})_6]I$	White needles	140–2		112
Hexakis(cyclohexylisocyano)-manganese(I) triodide	$[Mn(CNC_6H_{11})_6]I_3$	Colorless crystals	68–9		112
Hexakis(cyclohexylisocyano)-manganese(I) tetraphenylborate	$[Mn(CNC_6H_{11})_6][B(C_6H_5)_4]$	White needles	118–20		112

Hexakis(benzylisocyano)-manganese(I) iodide	$[Mn(CNC_7H_7)_6]I$	White crystals	184			112
Hexakis(benzylisocyano-manganese(I) triodide	$[Mn(CNC_7H_7)_6)I_3$	Red-brown crystals	115–6			112
Hexakis(benzylisocyano)-manganese(I) perchlorate	$[Mn(CNC_7H_7)_6]ClO_4$	White crystals	185–6			112
Hexakis(benzylisocyano)-manganese(I) tetraphenylborate	$[Mn(CNC_7H_7)_6][B(C_6H_5)_4]$	White crystals	128			112
Hexakis(phenylisocyano)-manganese(I) iodide	$[Mn(CNC_6H_5)_6]I$	Yellow crystals	216			109
Hexakis(phenylisocyano)-manganese(I) triodide	$[Mn(CNC_6H_5)_6]I_3$	Brown crystals	164 (dec.)			109
Hexakis(phenylisocyano)-manganese(I) perchlorate	$[Mn(CNC_6H_5)_6]ClO_4$	Yellow crystals	213 (dec.)			109
Hexakis(*p*-tolylisocyano)-manganese(I) iodide	$[Mn(CNC_7H_7)_6]I$	Pale yellow crystals	219	(1) (2)	-340×10^{-6} 29.2	109
Hexakis(*p*-tolylisocyano)-manganese(I) triodide	$[Mn(CNC_7H_7)_6]I_3$	Brown crystals	184 (dec.)	(1)	-790×10^{-6}	109
Hexakis(*p*-tolylisocyano)-manganese(I) perchlorate	$[Mn(CNC_7H_7)_6]ClO_4$	Pale yellow crystals	211 (dec.)	(1) (2)	-390×10^{-6} 30.0	109
Hexakis(*p*-anisylisocyano)-manganese(I) hydroxide	$[Mn(CNC_7H_7O)_6]OH$	Yellow crystals				110
Hexakis(*p*-anisylisocyano)-manganese(I) chloride	$[Mn(CNC_7H_7O)_6]Cl$	Yellow crystals	182			109

(continued)

TABLE IV (*continued*)

Name	Formula	Color and crystal form	M.p. or dec. temp., °C.	Other data[a]	Ref.
Hexakis(*p*-anisylisocyano)-maganese(I) bromide	$[Mn(CNC_7H_7O)_6]Br$	Yellow crystals	198		109
Hexakis(*p*-anisylisocyano)-manganese(I) iodide	$[Mn(CNC_7H_7O)_6]I$	Pale yellow crystals	227		109
Hexakis(*p*-anisylisocyano)-manganese(I) triiodide	$[Mn(CNC_7H_7O)_6]I_3$	Brown crystals	172	(1) -816×10^{-6}	109
Hexakis(*p*-anisylisocyano)-manganese(I) hydrogen carbonate	$[Mn(CNC_7H_7O)_6]HCO_3$	Pale yellow crystals	128 (dec.)		110
Hexakis(*p*-anisylisocyano)-manganese(I) chlorate	$[Mn(CNC_7H_7O)_6]ClO_3$	Pale yellow crystals	118 (dec.)		110
Hexakis(*p*-anisylisocyano)-manganese(I) perchlorate	$[Mn(CNC_7H_7O)_6]ClO_4$	Pale yellow crystals	213 (dec.)	(1) -440×10^{-6}	109
Hexakis(*p*-anisylisocyano)-manganese(I) tetrafluoroborate	$[Mn(CNC_7H_7O)_6]BF_4$	Pale yellow crystals	221		110
Hexakis(*p*-anisylisocyano)-manganese(I) tetraphenylborate	$[Mn(CNC_7H_7O)_6][B(C_6H_5)_4]$	Pale yellow crystals	164	(1) -710×10^{-6} (2) 19.1	110
Hexakis(*p*-anisylisocyano)-manganese(1) hexafluorophosphate	$[Mn(CNC_7H_7O)_6]PF_6$	Yellow crystals	207		110

Hexakis(*p*-chlorophenylisocyano)-manganese(I) iodide	[Mn$(CNC_6H_4Cl)_6$]I	Pale yellow crystals	247			109
Hexakis(*p*-chlorophenylisocyano)-manganese(I) triodide	[Mn$(CNC_6H_4Cl)_6$]I_3	Brown crystals	219 (dec.)			109
Hexakis(*p*-chlorophenylisocyano)-manganese(I) perchlorate	[Mn$(CNC_6H_4Cl)_6$]ClO_4	Yellow crystals	235 (dec.)			109
Hexakis(*p*-tolylisocyano)-manganese(II) nitrate	[Mn$(CNC_7H_7)_6$]$(NO_3)_2$	Blue crystals	114	(3)	1.69	92
Hexakis(*p*-tolylisocyano)-manganese(II) perchlorate	[Mn$(CNC_7H_7)_6$]$(ClO_4)_2$	Blue crystals	125	(3)	1.72	92
Hexakis(*p*-tolylisocyano)-manganese(II) tetrabromocadmiate	[Mn$(CNC_7H_7)_6$][$CdBr_4$]	Blue crystals	145	(3)	1.75	92
Hexakis(*p*-anisylisocyano)-manganese(II) tetraiodomercurate	[Mn$(CNC_7H_7O)_6$][HgI_4]	Blue crystals	132	(3)	1.72	92
Hexakis(*p*-anisylisocyano)-manganese(II) picrate	[Mn$(CNC_7H_7O)_6$][$OC_6H_2(NO_2)_3$]$_2$	Blue crystals	116	(3)	1.74	92

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[a] (1) Magnetic susceptibility, χ_M, of the solid at 20°C. (2) Molal conductivity, Λ_M, in $^1/_{5000}$ molar nitrobenzene solution at 18°C. (3) Uncorrected magnetic moment, μ.

less soluble triiodide, which was separated, purified, and then quantitatively reconverted into the iodide by shaking a chloroform solution with aqueous sodium thiosulfate.

The hexaisocyanomanganese(I) iodide, on reaction with silver oxide in aqueous alcoholic suspension, gives the corresponding hydroxide, $[Mn(CNR)_6]OH$. This is a stable crystalline substance, with strong alkaline character. The fact that the hydroxide of hexaisocyanomanganese(I) may be transformed into a stable crystalline bicarbonate, $[Mn(CNR)_6]HCO_3$, shows that its strength is comparable with that of the alkali hydroxides. In fact, only the alkali metals form bicarbonates that are stable in the solid state.

From the iodide by an exchange reaction, or from the hydroxide with the corresponding acid, many salts of hexaisocyanomanganese(I) ions were prepared (110), namely, chlorides, bromides, chlorates, perchlorates, bicarbonates, carbonates, tetrafluoroborates, tetraphenylborates, and hexafluorophosphates. Except when the anion itself is colored, these salts are colorless when R is an alkyl (methyl ethyl, cyclohexyl, benzyl) and yellow when R is an aryl (phenyl, *p*-tolyl, *p*-anisyl, *p*-chlorophenyl). They are soluble in methylene chloride, chloroform, and nitrobenzene, slightly soluble in benzene. The solubility in alcohol varies greatly, depending on the isocyanide and on the anion. They are all diamagnetic, as expected for hexacoordinated inner complexes of Mn^I, and in nitrobenzene solution behave as strong uni-univalent electrolytes. The tetraphenylborate of hexakis(arylisocyano)manganese(I), which is not dissociated in anhydrous benzene, has an extraordinarily high dipole moment (about 22 D.) (111).

The salts of hexaisocyanomanganese(I) are indefinitely stable to air both in the solid state and in solution, and melt, generally without decomposition, in a high temperature range (150–250°). This quite unusual thermal stability shows that the coordination of isocyanides to manganese(I) results in the stabilization not only of the unusual valence state for the metal, but also of isocyanides with respect to oxidation, polymerization, and rearrangement to cyanides.

It may be noticed that Cr^0, Mn^I, and Fe^{II} form a series of isoelectronic hexacoordinated isocyanide compounds—$Cr(CNR)_6$, $[Mn(CNR)_6]^+$, and $[Fe(CNR)_6]^{2+}$—in which, as in the analogous series—$[Co(CNR)_5]^+$, $Ni(CNR)_4$, and $[Cu(CNR)_4]^+$—the metal atom reached the E.A.N. (effective atomic number) of krypton.

2. Derivatives of Manganese(II)

The +2 oxidation state is usual for manganese in all its simple and in most of its complex salts. Yet the isocyanide derivatives of manganese(II) (92), in their general features as well as the manner of preparation, constitute a class of compounds quite apart from the other known complexes of divalent manganese. The solution of the hexakis(arylisocyano)manganese(I) salts, when treated with strong oxidants such as halogens, fuming nitric acid, and permanganic acid, develop an intense blue color because of the presence of the cation $[Mn(CNR)_6]^{2+}$. Of the salts of hexakis(arylisocyano)manganese(II), the tetrabromocadmiate, $[Mn(CNR)_6][CdBr_4]$, is the most easily obtained in a pure state. It is sparingly soluble and separates as blue crystals when an alcoholic solution of $[Mn(CNR)_6]Br$ is treated with bromine in presence of $CdBr_2$:

$$[Mn(CNR)_6]Br + {}^1/_2\,Br_2 + CdBr_2 \longrightarrow [Mn(CNR)_6][CdBr_4]$$

This compound can also be prepared by anodic oxidation of the univalent complex in alcoholic solution containing $CdBr_2$. The dinitrate, $[Mn(CNR)_6](NO_3)_2$, obtained by oxidation of the univalent nitrate with the calculated amount of concentrated nitric acid in glacial acetic acid, is readily soluble in alcohol. It is a very suitable intermediate for the preparation of other less soluble salts, namely, the tetraiodomercurate, the picrate, and the perchlorate. The perchlorate was also prepared by direct oxidation of the univalent complex with potassium permanganate in presence of perchloric acid.

The salts of hexakis(arylisocyano)manganese(II) are blue-violet crystalline substances, soluble in methylene chloride, chloroform, acetone, and glacial acetic acid, sparingly soluble in benzene and alcohol. In the solid state, and in solution in chloroform or glacial acetic acid, they are stable for several months. They are not affected by strong mineral acids, but decompose immediately in presence of alkali, probably according with the equation:

$$13\,[Mn(CNR)_6]^{2+} + 14\,OH^- \longrightarrow 12\,[Mn(CNR)_6]^+ + 6\,RNCO + Mn(OH)_2 + 6\,H_2O$$

An analogous reduction takes place in the presence of free isocyanide. Therefore, since the solutions of the hexakis(arylisocyano)manganese(II) salts are stable for quite a long time, it may be inferred that the stability constant of the cation $[Mn(CNR)_6]^{2+}$ is very high.

The hexakis(arylisocyano)manganese(II) salts are paramagnetic, with magnetic susceptibilities corresponding to one unpaired electron. This confirms, for the cation $[Mn(CNR)_6]^{2+}$, an octahedral structure with d^2sp^3 hybrid orbitals.

B. RHENIUM

The only work so far published on rhenium isocyanide compounds is that of Hieber and Schuster (48), who studied the substitution reaction of chloropentacarbonylrhenium(I) with *p*-tolyl isocyanide. Carrying out the reaction at 100° in petroleum ether, these authors obtained a very stable colorless crystalline product (dec. pt. over 200°), of composition corresponding to $ReCl(CO)_4(CNC_7H_7)$, which they formulated as $[Re(CO)_4(CNC_7H_7)]Cl$. However, this compound, which would be expected to be a strong uni-univalent electrolyte, shows only a very low electrical conductivity in acetone solution.

V. Isocyanide Compounds of the Group VIII Elements

A. IRON, RUTHENIUM, AND OSMIUM

Many interesting isocyanide compounds of iron, all derived from Fe^{II}, have long been known, and were extensively studied because of their relations with "ferrocyanides" (hexacyanoferrates). Recently, a number of dinitrosyldiisocyanoiron compounds, where iron displays a formally negative oxidation state, have been prepared. Very little has been done so far on ruthenium, and nothing on osmium. Of ruthenium, only one type of isocyanide compound has been described; they are derived from Ru^{II} and are very similar to the corresponding iron compounds.

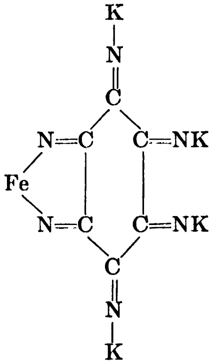
1. Iron

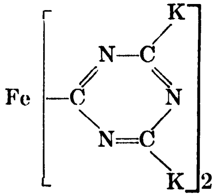
Isocyanide compounds of iron can be divided into three groups, according to the method used in their preparation: (*a*) compounds obtained by alkylation of hexacyanoferrates, (*b*) addition compounds of iron salts and isocyanides, and (*c*) substitution compounds of iron carbonyls and iron nitrosylcarbonyl with isocyanides.

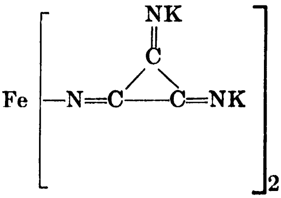
a. Compounds Obtained by Alkylation of Hexacyanoferrates

Though they are undoubtedly coordination compounds of isocyanides, some of them are formally considered as esters of hexacyanoferric(II) acid ("alkylferrocyanides"). The salts of the cation $[\mathrm{Fe(CNR)_6}]^{2+}$ (R = methyl, ethyl, *n*-propyl) are the most important compounds of this class. The so-called "alkylferrocyanides," of general formula $\mathrm{Fe(CN)_2(CNR)_4}$, are interesting because they occur in isomeric forms, the several structures of which have not yet been fully established. Owing to the complexity of the matter, a somewhat chronological order will be adopted in the description of these compounds.

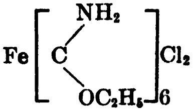
In the last decades of the nineteenth century a great deal of interest was shown by the organic chemists in the structure of potassium hexacyanoferrate(II) (potassium ferrocyanide) to which, among others, the following structures were attributed (30):







In order to determine its structure, many attempts were made to obtain organic derivatives of potassium hexacyanoferrate(II). The esterification of the corresponding free acid was attempted by Buff (1854) (5) who, by treating hexacyanoferric(II) acid with hydrogen chloride in alcohol, obtained a product which was formulated as $\mathrm{(C_2H_5)_4Fe(CN)_6 \cdot 2C_2H_5Cl \cdot 6H_2O}$. This product was later shown (2,19) to have the character of an iminoether, so that it could be written as



$$\mathrm{Fe}\left[\mathrm{C}\begin{matrix}\mathrm{NH_2}\\ \\ \mathrm{OC_2H_5}\end{matrix}\right]_6\mathrm{Cl_2}$$

TABLE V
Isocyanide Compounds of Iron

Name	Formula	Color and crystal form	M.p. or dec., temp., °C.	Ref.
Dinitrosylbis(methylisocyano)iron	$Fe(NO)_2(CNCH_3)_2$	Red-brown needles	150–200 (dec.)	46
Dinitrosylbis(ethylisocyano)iron	$Fe(NO)_2(CNC_2H_5)_2$	Red-brown needles	97–97.5 (sharp)	46
Dinitrosylbis(phenylisocyano)iron	$Fe(NO)_2(CNC_6H_5)_2$	Red-brown needles	140–3 (dec.)	46
Dinitrosylbis(*p*-tolylisocyano)iron	$Fe(NO)_2(CNC_7H_7)_2$	Brick red needles	180–2 (dec.)	73
Dinitrosylbis(*p*-anisylisocyano)iron	$Fe(NO)_2(CNC_7H_7O)_2$	Red-brown needles	197–9 (dec.)	73
Dinitrosylbis(*p*-chlorophenylisocyano)iron	$Fe(NO)_2(CNC_6H_7Cl)_2$	Red needles	197–9 (dec.)	73
Tetracarbonylmethylisocyanoiron(0)	$Fe(CO)_4(CNCH_3)$	Pale yellow tablets and prisms	31.5	45
Tetracarbonylethylisocyanoiron(0)	$Fe(CO)_4(CNC_2H_5)$	Pale yellow oil	−3	45
Tetracarbonylphenylisocyanoiron(0)	$Fe(CO)_4(CNC_6H_5)$	Pale yellow prisms	60.5–61	45
Tetracarbonyl(*p*-anisylisocyano)iron(0)	$Fe(CO)_4(CNC_7H_7O)$	Yellow needles	39–40	45

Bis(tetracarbonyliron)-μ-(1,4-diisocyanobenzene)	$(CO)_4FeCNC_6H_4NCFe(CO)_4$	Yellow crystals	Dec. > 100	45
Tricarbonylbis(methylisocyano)-iron(0)	$Fe(CO)_3(CNCH_3)_2$	Colorless leaflets	100–30 (dec.)	45
Tricarbonylbis(ethylisocyano)-iron(0)	$Fe(CO)_3(CNC_2H_5)_2$	Pale yellow leaflets and needles	65.5–66	45
Tricarbonylbis(*p*-anisylisocyano)-iron(0)	$Fe(CO)_3(CNC_7H_7O)_2$	Yellow crystals	89–91.5	45
Tricarbonyl(methylisocyano) (ethylisocyano)iron(0)	$Fe(CO)_3(CNCH_3)(CNC_2H_5)$	Pale yellow needles (from petroleum ether)	Dec. > 60	46
		Yellow square tablets (from methanol)		
Diiodotricarbonylmethylisocyanoiron(II)	$FeI_2(CO)_3(CNCH_3)$	Brown-red cubes	115 (dec.)	46
		Pleochroic prismatic needles		
Diiododicarbonyldi(methylisocyano)iron(II)	$FeI_2(CO)_2(CNCH_3)_2$	Dark brown leaflets	130 (dec.)	46
Diiodocarbonyltris(*p*-anisylisocyano)iron(II)	$FeI_2(CO)(CNC_7H_7O)_3$	Red-brown prisms and needles	Dec. > 140	46
Dichlorobis(*n*-amylisocyano)-iron(II)	$FeCl_2(CNC_5H_{11})_2$	Golden yellow powder		65
Dichlorobis(isoamylisocyano)-iron(II)	$FeCl_2(CNC_5H_{11})_2$	Golden yellow powder		65

(*continued*)

TABLE V (*continued*)

Name	Formula	Color and crystal form	M.p. or dec. temp., °C.	Ref.
Dichlorobis(phenylisocyano)-iron(II)	$FeCl_2(CNC_6H_5)_2$	Golden yellow powder		65
Bis(isoamylisocyano)iron(II) sulfate	$Fe(CNC_5H_{11})_2SO_4$	Intense yellow powder		65
Bis(phenylisocyano)iron(II) sulfate	$Fe(CNC_6H_5)_2SO_4$	Intense yellow powder		65
Dibromotetrakis(methylisocyano)iron(II)	$FeBr_2(CNCH_3)_4$	Brown substance		75
Diiodotetrakis(methylisocyano)-iron(II)	$FeI_2(CNCH_3)_4$	Brown substance		75
		Yellow substance		
Dicyanotetrakis(methylisocyano)iron(II)	$Fe(CN)_2(CNCH_3)_4$	Light yellow square tablets containing chloroform		
		Short yellow needles from hot methanol		32, 49, 91, 98
		White hexahydrate from water		
Aquodicyanotris(methylisocyano)iron(II)	$Fe(H_2O)(CN)_2(CNCH_3)_3$	Red substance		49
Pentacyanomethylisocyanoferric-(II) acid	$H_2[Fe(CN)_5(CNCH_3)]$			91

Hexakis(methylisocyano)iron(II) chloride trihydrate	$[Fe(CNCH_3)_6]Cl_2 \cdot 3H_2O$	Faintly yellow prisms		29,99
Adduct of hexakis(methylisocyano)iron(II) iodide with silver iodide	$[Fe(CNCH_3)_6]I \cdot 4AgI$	Grey crystalline powder		31
Hexakis(methylisocyano)iron(II) nitrate	$[Fe(CNCH_3)_6](NO_3)_2$	White crystals		31
Hexakis(methylisocyano)iron(II) hydrogensulfate	$[Fe(CNCH_3)_6](HSO_4)_2$	White crystals	220 (dec.)	28
Hexakis(methylisocyano)iron(II) methylsulfate	$[Fe(CNCH_3)_6](CH_3SO_4)_2$	Very hygroscopic white crystals		29
Hexakis(methylisocyano)iron(II) methylsulfate with methylsulfuric acid	$[Fe(CNCH_3)_6](CH_3SO_4)_2 \cdot 2CH_3HSO_4$	White crystals		28
Hexakis(methylisocyano)iron(II) hexachloroplatinate(IV)	$[Fe(CNCH_3)_6]PtCl_6$	White small crystals		29
Hexakis(methylisocyano)iron(II) triiodide	$[Fe(CNCH_3)_6](I_3)_2$	Dark shining crystals		31
Dicyanotetrakis(ethylisocyano)-iron(II)	$Fe(CN)_2(CNC_2H_5)_4$	Big colorless prisms	212–4 (dec.)	19
Tetrakis(methylisocyano)bis(ethylisocyano)iron(II) iodide, adduct with mercuric iodide	$[Fe(CNCH_3)_4(CNC_2H_5)_2]I_2 \cdot 2HgI_2$	α form: bright yellow crystals β form: pale yellow crystals		37
Pentacyano(ethylisocyano)ferric-(II) acid	$H_2[Fe(CN)_5(CNC_2H_5)]$			91

(continued)

TABLE V (*continued*)

Name	Formula	Color and crystal form	M.p. or dec. temp., °C.	Ref.
Dicyanotetrakis(*n*-propylisocyano)iron(II)	$Fe(CN)_2(CNC_3H_7)_4$	Colorless needles	100–7 (dec.)	91
Dichlorotetrakis(*p*-tolylisocyano)iron(II)	$FeCl_2(CNC_7H_7)_4$	Blue-violet needles from cold alcohol Light brown crystals from warm chloroform		75
Adduct with mercuric chloride	$FeCl_2(CNC_7H_7)_4 \cdot HgCl_2$	Red crystals		75
Adduct with mercuric bromide	$FeCl_2(CNC_7H_7)_4 \cdot HgBr_2$	Brick red crystals		75
Adduct with mercuric iodide	$FeCl_2(CNC_7H_7)_4 \cdot HgI_2$	Deep red crystals		75
Dibromotetrakis(*p*-tolylisocyano)iron(II)	$FeBr_2(CNC_7H_7)_4$	Deep blue crystals from cold alcohol Brown crystals from warm chloroform		75
Adduct with mercuric iodide	$FeBr_2(CNC_7H_7)_4 \cdot HgI_2$	Brown-red crystals		75
Diiodotetrakis(*p*-tolylisocyano)iron(II)	$FeI_2(CNC_7H_7)_4$	Emerald green prisms from cold alcohol Brown crystals from warm chloroform		75
Dithiocyanotetrakis(*p*-tolylisocyano)iron(II)	$Fe(SCN)_2(CNC_7H_7)_4$	Pale yellow crystals from cold alcohol Brick red crystals from warm alcohol		75
Dicyanotetrakis(*p*-chlorophenylisocyano)iron(II)	$Fe(CN)_2(CNC_6H_4Cl)$	White crystals from cold alcohol Pale yellow crystals from warm chloroform		75

Potassium dichlorotetrakis(*p*-isocyanobenzenesulfonate)ferrate(II)	$K_4[FeCl_2(CNC_6H_4SO_3)_4]$			105
Potassium dibromotetrakis(*p*-isocyanobenzenesulfonate)ferrate(II)	$K_4[FeBr_2(CNC_6H_4SO_3)_4]$	Yellow crystals		105
Potassium diiodotetrakis(*p*-isocyanobenzenesulfonate)ferrate(II)	$K_4[FeI_2(CNC_6H_4SO_3)_4]$	Light green crystals		105
Tetrakis(phenylisocyano)iron(II) perchlorate	$[Fe(CNC_6H_5)_4](ClO_4)_2$	Yellow needles		96
Tetrakis(*o*-tolylisocyano)iron(II) perchlorate	$[Fe(CNC_7H_7)_4](ClO_4)_2$	Yellow needles		96
Tetrakis(*p*-tolylisocyano)iron(II) perchlorate	$[Fe(CNC_7H_7)_4](ClO_4)_2$	Yellow needles	$\Lambda_\infty = 42$[a]	96
Tetrakis(*p*-chlorophenylisocyano)iron(II) perchlorate	$[Fe(CNC_6H_4Cl)_4](ClO_4)_2$	Yellow needles		96
Trichlorobis(ethylisocyano)iron(III)	$FeCl_3(C_2H_5NC)_2$	Yellow prisms		58
Trichlorotris(ethylisocyano)iron(III)	$FeCl_3(C_2H_5NC)_3$	Green-yellow leaflets		58
Oxotetrachlorotetrakis(ethylisocyano)diiron(III)	$Fe_2Cl_4O(C_2H_5NC)_4$	Yellow square tablets		58
Oxotetrachloropentakis(ethylisocyano)diiron(III)	$Fe_2Cl_4O(C_2H_5NC)_5$	Golden yellow crystals		58

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[a] Electrical conductivity in ohm^{-1} $cm.^{-2}$ in nitrobenzene solution at 20°.

The first true isocyanoiron derivative isolated in a pure state was Freund's "ethylferrocyanide" (1888) which was prepared by treating silver hexacyanoferrate(II) with ethyl iodide (19). At that time it was written as $(C_2H_5)_4Fe(CN)_6$, but since it gives off isocyanide on addition of potassium cyanide or on heating, and shows no electrical conductance in solution, it must be considered the dicyanotetrakis-(ethylisocyano)iron(II), $Fe(CN)_2(CNC_2H_5)_4$.

The methylation reaction of ferrocyanides was extensively studied by Hartley. The results of his research, described in a long series of papers (1910–1933), is summarized in the pages which follow. It must be stressed that here we attribute to Hartley's compounds the structure of isocyanide coordination compounds, which he took into consideration only in 1933.

The "esterification reaction" is carried out by refluxing for several hours a mixture of dry and finely powdered potassium hexacyanoferrate(II) with freshly distilled dimethyl sulfate (28). The reaction mixture is then filtered hot; on cooling the solution, a precipitate separates which, after recrystallization from methanol, has a composition corresponding to the formula $[Fe(CNCH_3)_6](HSO_4)_2$ (XVIII). This product is slightly soluble in alcohol and gives a precipitate with barium salts. From the mother liquor of XVIII, after removing the excess of dimethyl sulfate by evaporating it under reduced pressure, a crystalline mass is obtained. After recrystallization from methanol, it analyzes as $[Fe(CNCH_3)_6](CH_3SO_4)_2 \cdot 2\,CH_3HSO_4$ (XIX). This product is readily soluble in alcohol and gives no precipitate with barium salts. In vacuum it changes slowly into XVIII:

$$[Fe(CNCH_3)_6](CH_3SO_4)_2(CH_3HSO_4)_2 \longrightarrow [Fe(CNCH_3)_6](HSO_4)_2 + 2\,(CH_3)_2SO_4$$

When the methylation reaction was carried out under different conditions, another compound was obtained—$[Fe(CNCH_3)_6](CH_3SO_4)_2$ (XX). The compounds XVIII, XIX, and XX give the same precipitate, $[Fe(CNCH_3)_6][PtCl_6]$, with hexachloroplatinic(IV) acid, which proves that they are salts of the same cation, $[Fe(CNCH_3)_6]^{2+}$.

The above-described methylation reaction can be written as follows:

$$[Fe(CN)_6]^{4-} + 6\,(CH_3)^+ \longrightarrow [Fe(CNCH_3)_6]^{2+}$$

thus stressing the intimate relations between cyanometallates and isocyanide coordination compounds.

The salt XVIII is the most easily obtained because of its sparing solubility, and is formed also by treating with sulfuric acid an alcoholic solution of XIX and XX.

By neutralizing a solution of XVIII with barium hydroxide, the sulfate (XXI) is formed. This can be isolated but, being very soluble, cannot be obtained easily in a pure state. From the sulfate (XXI) the chloride (XXII) can be prepared as follows. A solution of the sulfate is treated with a slight excess of barium chloride, filtered, and evaporated to dryness under reduced pressure. The residue is extracted with alcohol and the alcoholic solution precipitated with ether. The chloride separates in a bulky colorless crystalline mass:

$$[Fe(CNCH_3)_6](HSO_4)_2 + Ba(OH)_2 \longrightarrow \underset{(XXI)}{[Fe(CNCH_3)_6]SO_4} + BaSO_4 + 2\,H_2O$$

$$[Fe(CNCH_3)_6]SO_4 + BaCl_2 \longrightarrow \underset{(XXII)}{[Fe(CNCH_3)_6]Cl_2} + BaSO_4$$

According to Hölzl (1927) (49), the chloride (XXII) can also be prepared by boiling an aqueous solution of XVIII, XIX, and XX with HCl or $BaCl_2$.

Hexakis(methylisocyano)iron(II) chloride is the only isocyanide derivative, the structure of which has been fully determined. Powell and Bartindale found (1945) (99) for the carbon–iron distance a value of 1.85 A., rather lower than the value calculated from the covalent radii of the elements, and very near to that in $Fe(CO)_5$. From this value, the amount of double bonding in the carbon–iron link has been estimated to be about 50%. It was also shown that the bonds $Fe—C—N—CH_3$ are not on a straight line, but there is a bend with a C—N—C angle of 7 degrees.

By heating under reduced pressure at 130–150°, the chloride of hexakis(methylisocyano)iron(II) is transformed into the "methylferrocyanide," that is, into the dicyanotetrakis(methylisocyano)-iron(II) (XXIII), which is the methyl analogue of Freund's "ethylferrocyanide":

$$[Fe(CNCH_3)_6]Cl_2 \xrightarrow{150^\circ} Fe(CN)_2(CNCH_3)_4 + 2\,CH_3Cl$$

This compound cannot be prepared directly from $Ag_4[Fe(CN)_6]$ and CH_3I because, even with a defect of CH_3I, an addition compound between silver iodide and the iodide of hexakis(methylisocyano)-iron(II) is obtained (31):

$$Ag_4[Fe(CN)_6] + 6\,CH_3I \longrightarrow [Fe(CNCH_3)_6]I_2\cdot 4\,AgI$$

This double salt is decomposed by dilute nitric acid and silver nitrate:

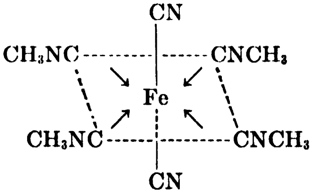
$$[Fe(CNCH_3)_6]I_2\cdot 4\,AgI \xrightarrow[AgNO_3]{HNO_3} [Fe(CNCH_3)_6](NO_3)_2 + 6\,AgI$$

An analogous addition compound is formed in the reaction between silver hexacyanoferrate(II) and ethyl iodide (37), carried out at ordinary temperature. The adduct $[Fe(CNC_2H_5)_6]I_2\cdot 4AgI$ gives with silver nitrate the salt $[Fe(CNC_2H_5)_6](NO_3)_2$ and with sulfuric acid the hydrogen sulfate, $[Fe(CNC_2H_5)_6](HSO_4)_2$.

In the reaction between silver hexacyanoferrate(III) (ferricyanide) and methyl iodide (31) some hexakis(methylisocyano)iron(II) triiodide is formed, together with the addition product with silver iodide:

$$4\,Ag_3[Fe(CN)_6] + 24\,CH_3I \longrightarrow 3\,[Fe(CNCH_3)_6]I_2\cdot 4\,AgI + [Fe(CNCH_3)_6](I_3)_2$$

The dicyanotetrakis(methylisocyano)iron(II), mentioned above, is not a unique product, but a mixture of two isomers, called α and β, which can be separated owing to their different solubilities in chloroform (32). By alkylation with methyl iodide the two isomers give the same cation, $[Fe(CNCH_3)_6]^{2+}$; when ethyl iodide instead of methyl iodide is used, two different cations are obtained (37). These facts, together with the known molecular weights in solution, agree with the suggestion (23) that the α- and β-forms of the "tetramethylferrocyanide" are *cis* and *trans* isomers, and Powell and Stanger showed by X-ray examination that the β-form is the *trans* hexacoordinated compound (98):



It may be interesting to recall that during these X-ray investigations on isocyanide compounds Powell observed that the isocyanide–iron bonds were strictly similar to those of the mononuclear carbonyls. Considering that one of the reasons for the stability of compounds of this type is the attainment of the E.A.N. of the next inert gas, he fore-saw that compounds such as $Mn(CN)(CNCH_3)_5$ and $Cr(CNCH_3)_6$ should be capable of existence. In fact, isocyanide compounds very similar to those predicted by Powell were obtained later (see Sections III-A and IV-A).

In addition to the "α- and β-tetramethylferrocyanides" of Hartley, already mentioned (32), other supposed isomers and similar compounds have been described, but in my opinion their identification and formulation are rather uncertain. Hölzl repeated (49) the preparation of the "methylferrocyanides" in a way slightly different from Hartley's and obtained two substances, which he called α and β and considered to be the same as Hartley's α- and β-isomers. For the former he objected to the structure of dicyanotetrakis(methylisocyano)iron(II) and proposed a structure of dicyanide of tetrakis(methylisocyano)iron(II). However Hölzl's β-isomer was later recognized (37) to be different from Hartley's, for which a structure of *trans*-dicyanotetrakis(methylisocyano)iron(II) was found by X-ray investigation (98). Hölzl's β-isomer, according to a proposal of Meyer (91), has since been called γ. The "γ-methylferrocyanide" is a substance that is more soluble in water then the β-form, is nearly insoluble in chloroform, and behaves as an electrolyte.

There are two other substances with a composition similar to the α-, β-, and γ-isomers. One was obtained by Meyer and co-workers (91) by treating hexacyanoferric(II) acid with diazomethane. It was a salt-like product which analyzed as $(CH_3)_4Fe(CN)_6 \cdot H_2O$ and was formulated as a cyanide of cyanoaquotetrakis(methylisocyano)iron(II), $[Fe(CN)(H_2O)(CNCH_3)_4]CN$. The other was obtained by Hölzl (49), by extracting with aqueous instead of anhydrous methanol the solid mass obtained in the preparation of $[Fe(CNCH_3)_6]Cl_2$. The aqueous alcoholic solution was evaporated under reduced pressure and the residue heated under vacuum at 150–160°; the substance thus obtained was an electrolyte, of composition corresponding to $Fe(CN)_2(CNCH_3)_4 \cdot 4H_2O \cdot 2CH_3OH$. It was formulated by Hölzl as a dicyanide of bismethanolotetrakis(methylisocyano)iron(II) tetrahydrate, $[Fe(CH_3OH)_2(CNCH_3)_4](CN)_2 \cdot 4H_2O$, but it seems at least very strange that a compound obtained by heating under vacuum should contain methanol and water.

From the reaction between silver hexacyanoferrate(II) and *n*-propyl iodide Hölzl could isolate (49) only one of the possible isomers of the dicyanotetrakis(*n*-propylisocyano)iron(II):

$$Ag_4[Fe(CN)_6] + 4\ C_3H_7I \longrightarrow Fe(CN)_2(CNC_3H_7)_4 + 4\ AgI$$

The product obtained is a white crystalline substance, soluble in alcohol and chloroform.

Hölzl described also some hydrolysis products of "methylferrocyanide"; the best defined of these is a red (?) dicyanoaquotris-(methylisocyano)iron(II), $Fe(CN)_2(H_2O)(CNCH_3)_3$ (49).

Finally Meyer and co-workers (91) obtained, by treating with diazomethane and diazoethane an ethereal solution of hexacyanoferric-(III) acid, compounds in which only one cyanide group had been alkylated. The free acids $H_2[Fe(CN)_5(CNCH_3)]$ and $H_2[Fe(CN)_5(CNC_2H_5)]$ are very unstable, but their silver and copper salts, and in general the salts with cations of heavy metals, though not easily obtained in a pure state, seem to be quite stable.

b. Addition Compounds of Iron Salts and Isocyanides

The most interesting compounds of this class derive from iron(II) salts; the few known derivatives of iron(III) are rather unstable and have no remarkable features. The compounds obtained by direct reaction of iron(II) salts and isocyanides contain at most four molecules of ligand; no hexaisocyanide derivatives of the type described in Section V-A-1-a have been obtained so far. In these compounds the coordination number of iron can be either four, as in $[Fe(CNR)_4](ClO_4)_2$, or six, as in $FeCl_2(CNR)_4$. Both the tetra- and hexacoordinated complexes are diamagnetic.

According to work of Hofmann and Bugge (58), it is possible to prepare addition compounds of $FeCl_3$ and isocyanides, though they are unstable and completely hydrolyzed by water. On the other hand, the analogous addition compounds of $FeCl_2$ are said to be quickly oxidized by air to derivatives of Fe(III).

The following compounds are described: $FeCl_3 \cdot 2C_2H_5NC$ and $FeCl_3 \cdot 3C_2H_5NC$, yellow hygroscopic crystals, readily decomposed by alcohols, obtained by addition of isocyanides to an ethereal solution of $FeCl_3$; $Fe_2Cl_4O \cdot 4C_2H_5NC$ and $Fe_2Cl_4O \cdot 5C_2H_5NC$, unstable yellow crystalline substances, obtained from a methanolic or ethanolic solution of $FeCl_2$ and ethyl isocyanide (in presence of air as oxidizing agent). They give both the reactions of Fe^{3+} and Cl^- free ions.

The real existence of these derivatives of iron(III) formed by spontaneous oxidation from iron(II) compounds should, however, be accepted with reserve. In fact, the reported tendency of the isocyanide derivatives to be oxidized by air is in contrast to the remarkable stability of both the hexakis(alkylisocyano)iron(II) salts of Hartley (28–30) and the tetraisocyanide compounds of Malatesta and co-workers (75).

By reacting anhydrous ferrous sulfate or ferrous chloride with alkyl and aryl isocyanides, without solvent or in ethereal suspension, Malatesta obtained (65) some addition compounds of composition corresponding to $FeSO_4 \cdot 2CNR$ and $FeCl_2 \cdot 2CNR$. These are yellow crystalline powders, extremely soluble in water, alcohol, and polar organic solvents, by which they are readily decomposed. Their solutions give immediately the reactions of SO_4^{-} and Cl^{-}, but not those of the Fe^{2+} ion. Their structures have not been investigated further.

When the reaction between iron(II) salts and isocyanides was carried out in alcoholic or aqueous alcoholic solution, very stable compounds of composition corresponding to $FeX_2(CNR)_4$ (X = Cl, Br, I, SCN; R = alkyl or aryl) were obtained (Malatesta and co-workers (75)). All these compounds occur in two forms. One, obtained by rapid precipitation from cold solution, is intensely colored (green or blue) and sparingly soluble; the other, obtained from the former by boiling it in presence of solvents, or directly by precipitation from hot solutions, is brown or yellow and very soluble in organic solvents. Both forms are diamagnetic and nonelectrolytes, and, although their molecular weights have not been determined, they can be assumed to be monomeric hexacoordinate *cis-trans* isomers, of the same type as the "α- and β-methylferrocyanides" of Hartley.

The aromatic analogues of "methylferrocyanides" could not be prepared directly from $Fe(CN)_2$ and aryl isocyanides, probably because of the highly complex structure of the so-called ferrous cyanide. However, by reacting the dibromotetrakis(*p*-chlorophenylisocyano)-iron(II) with silver cyanide, two substances were obtained, one white and practically insoluble in chloroform, the other yellow and soluble in chloroform. Both had a composition corresponding to $Fe(CN)_2(CNC_6H_4Cl)_4$, and it is possible, though not proved, that they are the aromatic analogues of "methylferrocyanides."

Sacco and Coletti (105) by reaction of ferrous halogenides with the potassium salts of *p*-isocyanobenzenesulfonic acid in alcoholic solution, obtained compounds of formula $K_4[FeX_2(CNC_6H_4SO_3)_4]$. These are crystalline substances, soluble in water but insoluble in organic solvents, by which they are slowly decomposed.

The dihalogenotetraisocyanoiron(II) compounds form stable and well-defined adducts with mercuric halides (75). These compounds, of general formula $FeX_2(CNR)_4 \cdot HgX'_2$ (X and X′ are the same or different halogen atoms) are red or brown-red crystalline substances, readily soluble in organic solvents. They can be considered similar to the addition compounds of hexakis(methylisocyano)iron(II) salts and silver or mercury(II) halides.

An interesting series of compounds was prepared by Padoa, by direct reaction of isocyanides and ferrous perchlorate, without solvents (96). The reaction mixture, recrystallized several times from methanol, gave pale yellow crystals, of composition corresponding to $[Fe(CNR)_4](ClO_4)_2$ (R= phenyl, *p*-tolyl, *p*-chlorophenyl). These compounds are soluble in water, alcohol, chloroform, and nitrobenzene, insoluble in benzene and ether. They have the character of strong uni-divalent electrolytes and are diamagnetic. They were attributed a tetracoordinated structure implying square planar dsp^2 hydrid orbitals, and were the first example of 'inner complexes" for tetracoordinated iron(II).

c. Substitution Compounds of Iron Carbonyls and Iron Nitrosylcarbonyls

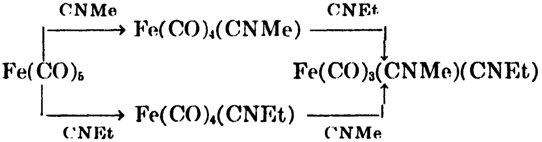
(*1*) *Derivatives of Pure Carbonyls.* Unlike nickel tetracarbonyl and dicobalt octacarbonyl, iron pentacarbonyl shows very low reactivity toward isocyanides. No reaction takes place in the cold when $Fe(CO)_5$ is treated with isocyanides, and the first attempts to carry out the reaction at higher temperature gave only "sticky crusts that could not be recrystallized" (62). The reaction between iron dodecacarbonyl and isocyanides, instead, proceeds rapidly and neatly (45). The products are well-defined crystalline substances, corresponding to the substitution of one or two carbon monoxide molecules of $Fe(CO)_5$ by isocyanides:

$$[Fe(CO)_4]_3 + 3\,RNC \longrightarrow 3\,[Fe(CO)_4(CNR)]$$
$$[Fe(CO)_4]_3 + 6\,RNC \longrightarrow 3\,[Fe(CO)_3(CNR_2] + 3\,CO$$

The same products can be obtained from iron pentacarbonyl at 70–90°, provided the isocyanide does not exceed the amount required by the above reactions.

Carbonylisocyanoiron compounds are yellow crystalline substances with low melting points. The monosubstituted compounds are remarkably volatile, though less then the corresponding pure carbonyl, and are usually purified by sublimation in high vacuum. The disubstituted compounds are still volatile, but to a much lower extent. Both the mono- and disubstituted compounds are photosensitive, moderately stable to air, soluble in organic solvents, and insoluble in water. Their solutions have no electrical conductance, and the molecular weights in solution correspond to a monomeric structure.

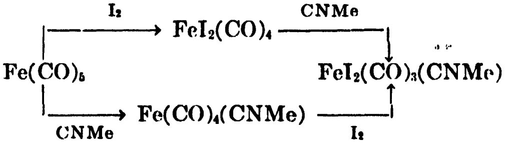
Owing to the trigonal bipyramidal structure attributed to iron pentacarbonyl (17), the compounds of the type $Fe(CO)_3(CNR)_2$ should be able to exist in stereoisomeric forms. Hieber (46), however, obtained only one mixed disubstituted product, operating in the following two ways:



If the bipyramidal structure is accepted for iron pentacarbonyl, then the fact that no stereoisomers are obtained in the above reactions can be explained by assuming either that the two isocyanide molecules enter in equivalent positions or that they are easily interchanged.

(*2*) *Derivatives of Diiodotetracarbonyliron(II).* The substitution reaction of diiodotetracarbonyliron and isocyanides was studied by Hieber and co-workers (46). According to the amount and the type of isocyanide used, mono-, di-, and trisubstituted derivatives were obtained, with the respective formulas $FeI_2(CO)_3(CNR)$, $FeI_2(CO)_2(CNR)_2$, and $FeI_2(CO)(CNR)_3$. The last compound represents the maximum degree of substitution attainable in this reaction.

The monosubstituted products could also be prepared by heating the tetracarbonylisocyanide compounds with iodine. In this case, too, the products obtained by the two methods are identical:



The substitution products of diiodotetracarbonyliron with isocyanides are more stable then the iodocarbonyl itself. They are brown crystalline substances, soluble in organic solvents, and they decompose without melting in the range 130–200°. Unlike the diiodotetracarbonyliron, they were not obtained in stereoisomeric forms.

(*3*) *Derivatives of Dinitrosyldicarbonyliron.* Dinitrosyldicarbonyliron, $Fe(NO)_2(CO)_2$, which is isoelectronic with $Ni(CO)_4$, reacts with isocyanides much more readily than iron pentacarbonyl. The reaction consists in the diplacement of the two CO molecules by two isocyanides, to give the dinitrosyldiisocyanoiron compounds (method *1*):

$$Fe(NO)_2(CO)_2 + 2\,RNC \longrightarrow Fe(NO)_2(CNR)_2 + 2\,CO$$

The same products can also be obtained (*2*) from nitrosyl compounds of iron with isocyanides and (*3*) from the dihalogenotetraisocyanoiron compounds with hydroxylamine.

The compounds containing methyl and ethyl isocyanide were prepared with the first method, carrying out the reaction in inert atmosphere; the compounds containing aryl isocyanides can also be prepared by method *1*, but were first obtained with methods *2* and *3* (71,73).

The reactions of isocyanides with $K_2[Fe_2(NO)_4S_2]$, red Roussin's salt, and with $NH_4[Fe(NO)_2(S_2O_3)]$ are examples of method *2*:

$$K_2[Fe_2(NO)_4S_2] + 4\,RNC \longrightarrow 2\,[Fe(NO)_2(CNR)_2] + K_2S_2$$

$$NH_4[Fe(NO)_2(S_2O_3)] + 2\,RNC \longrightarrow 2\,[Fe(NO)_2(CNR)_2] + {}^1/_2\,(NH_4)_2S_4O_6$$

The reaction takes place in alcohol upon gently warming the mixture. The products can be purified by dissolution in benzene followed by reprecipitation with alcohol.

Method *3* is based on the fact, pointed out by Nast (93), that hydroxylamine in alkaline solution undergoes a disproportionation reaction:

$$2\,NH_2OH \longrightarrow NH_3 + NOH + H_2O$$

$$NOH \longrightarrow NO^- + H^+$$

$$FeX_2(CNR)_4 + 2\,NO^- \longrightarrow Fe(NO)_2(CNR)_2 + 2\,X^- + 2\,CNR$$

This reaction takes place slowly in alcoholic solution.

The dinitrosyldiisocyanoiron compounds are beautifully crystalline substances, of colors varying from orange to dark red. They are stable in the solid state if kept in an open container; in a stoppered one an autocatalytic decomposition occurs. These compounds are soluble in polar organic solvents and diamagnetic. The dipole moments of the *p*-tolyl- and *p*-chlorophenylisocyanide derivatives have been measured in benzene solution, and are rather high (about 6 D.) (73).

2. Ruthenium

The isocyanide compounds of ruthenium prepared so far (82,87) are all derivatives of $Ru(^{II})$ with the general formula $RuX_2(CNR)_4$ ($X = Cl, Br, I, Cn$; $R =$ alkyl and aryl) (Malatesta and co-workers). Like the analogous iron compounds, they are all diamagnetic.

The dichloro and dibromo derivatives were prepared (82) by boiling in alcohol a mixture of $RuCl_3$ or $RuBr_3$ and an excess of alkyl or aryl isocyanide. The reaction can be written as follows:

$$RuCl_3 + 4\,RNC + e^- \longrightarrow RuCl_2(CNR)_4 + Cl^-$$

The reducing agent may be either the solvent or the excess of isocyanide itself. On cooling the alcoholic solution, the products separated in a crystalline state. The diiodo and dicyano derivatives (87) could not be obtained in this way probably because of the polymeric structure of RuI_3 and $Ru(CN)_3$.

The iodo compounds were prepared from the diiododicarbonylruthenium(II), $RuI_2(CO)_2$, by warming it with pure aryl isocyanide. From the reaction mixture the product was obtained by extracting it with hot alcohol. No well-defined compounds with alkyl isocyanides have been obtained by this method.

The compounds $RuX_2(CNR)_4$ ($X =$ halogen) occur in two forms of different colors and solubilities, which in some cases could not be separated. Both forms are nonelectrolytes and monomeric in solution, and it seems likely that they are the *cis-trans* isomers of dihalogenotetrakis(isocyano)ruthenium(II).

The dicyanide derivatives were prepared either by treating the corresponding chloro and bromo compounds with silver cyanide, in chloroform suspension, or by alkylation of hexacyanoruthenic(II) acid, $H_4[Ru(CN)_6]$. The first method gave satisfactory results only with compounds containing alkyl isocyanides. The alkylation reaction was carried out with diazomethane according to a method proposed by Meyer (89,90), both on the free hexacyanoruthenic(II) acid

TABLE VI
Isocyanide Compounds of Ruthenium

Name	Formula	Color and crystal form	M.p. or dec. temp., °C.	Ref.
Dichlorotetrakis(methylisocyano)ruthenium(II)	$RuCl_2(CNCH_3)_4$	Grey crystals from isopropyl ether Yellow-green crystals from cold alcohol		87
Dibromotetrakis(methylisocyano)ruthenium(II)	$RuBr_2(CNCH_3)_4$	Red and yellow prisms (not separated)		87
Dicyanotetrakis(methylisocyano)-ruthenium(II)	$Ru(CN)_2(CNCH_3)_4$	White crystals		87
Hydroxocyanotetrakis(methylisocyano)-ruthenium(II)	$Ru(CN)(OH)(CNCH_3)_4$	Pale yellow star-like crystals		87
Dichlorotetrakis(ethylisocyano)-ruthenium(II)	$RuCl_2(CNC_2H_5)_4$	Light blue crystals from cold alcohol Yellow crystals from ethyl ether		82
Dibromotetrakis(ethylisocyano)-ruthenium(II)	$RuBr_2(CNC_2H_5)_4$	Golden yellow crystals from cold alcohol Brick red crystals from isopropyl ether		87

Dicyanotetrakis(ethylisocyano)-ruthenium(II)	$Ru(CN)_2(CNC_2H_5)_4$	White crystals		87
Dichlorotetrakis(*p*-tolylisocyano)-ruthenium(II)	$RuCl_2(CNC_7H_7)_4$	Green prisms Yellow prisms from acetone	256 (dec.)	82
Dibromotetrakis(*p*-tolylisocyano)-ruthenium(II)	$RuBr_2(CNC_7H_7)_4$	Dark green octahedral crystals	266 (dec.)	82
Diiodotetrakis(*p*-tolylisocyano)-ruthenium(II)	$RuI_2(CNC_7H_7)_4$	Colorless crystals		87
Dicyanotetrakis(diphenylmethylisocyano)-ruthenium(II)	$Ru(CN)_2(CNC_{13}H_{11})_4$	Colorless crystals		87
Dichlorodiiodotetrakis(*p*-tolylisocyano)-ruthenium	$RuCl_2I_2(CNC_7H_7)_4$	Red crystals	159 (dec.)	82
Chlorotriiodotetrakis(*p*-tolylisocyano)-ruthenium	$RuClI_3(CNC_7H_7)_4$	Red crystals	159 (dec.)	82
Dibromononaiodotetrakis(*p*-tolylisocyano)ruthenium	$RuBr_2I_9(CNC_7H_7)_4$	Black-green prisms		82

in anhydrous ether and on its etherate in ethyl ether. In the first case a compound of formula $Ru(CN)_2(CNCH_3)_4$ was obtained which was identical with that prepared from $RuBr_2(CNCH_3)_4$ with AgCN; in the other case a compound, $Ru(CN)(OH)(CNCH_3)_4$, was isolated, which can be considered a hydrolysis product of the dicyano derivative.

Using diphenyldiazomethane, $(C_6H_5)_2CN_2$, instead of diazomethane, the compound $Ru(CN)_2[CN{\cdot}CH(C_6H_5)_2]_4$ was obtained. This derives from the diphenylmethylisocyanide, which has not been isolated in the free state. It is remarkable that all these dicyano derivatives have been obtained in only one form, usually colorless crystals, soluble in chloroform, very sparingly soluble in alcohol.

On treating with bromine and iodine, the compounds $RuX_2(CNR)_4$ give crystalline products of dark colors, probably polybromides and polyiodides, which, on boiling in solution, are reconverted into the starting compounds.

B. COBALT, RHODIUM, AND IRIDIUM

The isocyanide derivatives of cobalt and rhodium have been extensively studied, while no research on iridium has been published so far. Cobalt and rhodium form isocyanide compounds in which they display the oxidation states three, two, and one, and cobalt is known to give also nitrosylisocyanide compounds in which the formal oxidation state is -1. All these compounds are remarkably stable. It may be interesting to notice that the divalent derivatives, which would be expected to be paramagnetic even with an "inner" structure, are in many cases diamagnetic, but it is not always clear how this state of diamagnetism is reached.

The similarity previously observed among the isocyanide compounds of the elements in different periods of each group here becomes less marked; for instance, to the pentacoordinated cobalt(I), $[Co(CNR)_5]^+$, there corresponds the tetracoordinated rhodium(I) cation, $[Rh(CNR)_4]^+$. In the nickel group there is a still greater difference in behavior among nickel, palladium, and platinum.

1. Cobalt

As in the case of iron, isocyanide compounds of cobalt will be divided into three main classes, according to the method of preparation: (*a*) compounds obtained by alkylation of hexacyanocobaltates-

TABLE VII

Isocyanide Compounds of Cobalt

Name	Formula	Color and crystal form	M.p. or dec. temp., °C.	Other data[a]	Ref.
Nitrosylcarbonylbis(*p*-tolylisocyano)cobalt	$[Co(NO)(CO)(CNC_7H_7)_2]$	Orange-red needles	156–9 (dec.)		73
Nitrosyltris(*p*-tolylisocyano)cobalt	$[Co(NO)(CNC_7H_7)_3]$	Red needles	157–60 (dec.)	(1) 5.29 D	73
Nitrosyltris(*p*-anisylisocyano)cobalt	$[Co(NO)(CNC_7H_7O)_3]$	Orange needles	130–4 (dec.)	(1) 5.78 D	73
Nitrosyltris(*p*-chlorophenylisocyano)cobalt	$[Co(NO)(CNC_6H_4Cl)_3]$	Orange needles	107–8 (dec.)	(1) 3.33 D	73
Pentakis(methylisocyano)cobalt(I) perchlorate	$[Co(CNCH_3)_5]ClO_4$	Yellow needles		(2) -96×10^{-6}	113
Pentakis(methylisocyano)cobalt(I) tetracarbonylcobaltate(−I)	$[Co(CNCH_3)_5][Co(CO)_4]$	Pale yellow needles			103
Pentakis(phenylisocyano)cobalt(I) iodide	$[Co(CNC_6H_5)_5]I$	Orange prisms		(2) -140×10^{-6}	72
Adduct with mercuric iodide	$Co(CNC_6H_5)_5I \cdot HgI_2$	Brown leaflets	115 (dec.)	(2) -249×10^{-6}	72
Pentakis(phenylisocyano)cobalt(I) nitrate	$[Co(CNC_6H_5)_5]NO_3$	Pale yellow crystals			77
Pentakis(phenylisocyano)cobalt(I) chlorate	$[Co(CNC_6H_5)_5]ClO_3$	Pale yellow prisms			77

(continued)

TABLE VII (*continued*)

Name	Formula	Color and crystal form	M.p. or dec. temp., °C.	Other data[a]	Ref.
Pentakis(phenylisocyano)-cobalt(I) perchlorate	$[Co(CNC_6H_5)_5]ClO_4$	Yellow needles		(2) -320×10^{-6}	72
Pentakis(*o*-tolylisocyano)-cobalt(I) perchlorate	$[Co(CNC_7H_7)_5]ClO_4$	Golden yellow needles		(2) -372×10^{-6}	72
Adduct of pentakis(*p*-tolylisocyano)cobalt(I) bromide with mercuric bromide	$Co(CNC_7H_7)_5Br \cdot HgBr_2$	Yellow leaflets	155–60 (dec.)	(2) -210×10^{-6}	72
Pentakis(*p*-tolylisocyano)-cobalt(I) iodide	$[Co(CNC_7H_7)_5]I$	Orange-red prisms	99–100 (dec.)	(2) -270×10^{-6} (3) 17.85	72
Adduct with mercuric iodide	$Co(CNC_7H_7)_5I \cdot HgI_2$	Brick red prisms	120–5 (dec.)	(2) -289×10^{-6}	72
Adduct with mercurous iodide (2:1)	$\{Co(CNC_7H_7)_5I\}_2 \cdot Hg_2I_2$	Golden yellow needles	110–5 (dec.)	(2) -590×10^{-6}	72
Adduct with mercurous iodide (1:1)	$Co(CNC_7H_7)_5I \cdot Hg_2I_2$	Orange prisms	154 (dec.)	(2) -320×10^{-6}	72
Adduct with silver iodide	$Co(CNC_7H_7)_5I \cdot AgI$	Amber-colored crystals	150 (dec.)	(2) -210×10^{6}	72
Adduct with cadmium iodide (2:1)	$\{Co(CNC_7H_7)_5I\}_2 \cdot CdI_2$	Tobacco-colored prisms	165–70 (dec.)	(2) -512×10^{-6}	72
Pentakis(*p*-tolylisocyano)-cobalt(I) perchlorate	$[Co(CNC_7H_7)_5]ClO_4$	Golden yellow needles		(1) 11.2 D (2) -450×10^{-6} (4) 22.8	72
Adduct with mercuric iodide	$[Co(CNC_7H_7)_5]ClO_4 \cdot HgI_2$	Deep red prisms			72

Pentakis(*p*-tolylisocyano)-cobalt(I) tetracarbonyl-cobaltate(−I)	$[Co(CNC_7H_7)_5][Co(CO)_4]$	Brown-yellow needles				103
Pentakis(*p*-chlorophenyliso-cyano)cobalt(I) iodide	$[Co(CNC_6H_4Cl)_5]I$	Yellow-orange prisms		(2)	-30×10^{-6}	72
Pentakis(*p*-chlorophenyliso-cyano)cobalt(I) nitrate	$[Co(CNC_6H_4Cl)_5]NO_3$	Pale yellow prisms				77
Pentakis(*p*-chlorophenyliso-cyano)cobalt(I) chlorate	$[Co(CNC_6H_4Cl)_5]ClO_3$	Pale yellow prisms				77
Pentakis(*p*-chlorophenyliso-cyano)cobalt(I) perchlorate	$[Co(CNC_6H_4Cl)_5]ClO_4$	Yellow needles		(2)	-335×10^{-6}	72
Pentakis(*p*-chlorophenyliso-cyano)cobalt(I) tetracar-bonylcobaltate(−I)	$[Co(CNC_6H_4Cl)_5][Co(CO)_4]$	Yellow needles				103
Pentakis(3-chloro-2-methyl-phenylisocyano)cobalt(I) perchlorate	$[Co(CNC_7H_6Cl)_5]ClO_4$	Yellow needles		(2)	-361×10^{-6}	72
Pentakis(*β*-naphthylisocyano)-cobalt(I) iodide	$[Co(CNC_{10}H_7)_5]I$	Yellow-orange prisms				72
Tetrakis(methylisocyano)-cobalt(II) tetrachloro-cobaltate(II)	$[Co(CNCH_3)_4][CoCl_4]$	Green crystals	220 (dec.)	(2) (5)	8940×10^{-6} 524	113
Tetrakis(methylisocyano)-cobalt(II) tetrabromoco-baltate(II)	$[Co(CNCH_3)_4][CoBr_4]$	Green crystals	243 (dec.)	(2) (5)	9166×10^{-6} 470	113

(continued)

TABLE VII (*continued*)

Name	Formula	Color and crystal form	M.p. or dec. temp., °C.	Other data[a]	Ref.
Tetrakis(methylisocyano)-cobalt(II) tetrathiocyano-cobaltate(II)	$[Co(CNCH_3)_4][Co(SCN)_4]$	Green crystals	158 (dec.)	(2) 7640 × 10^{-6}	113
Dichlorobis(ethylisocyano)-cobalt(II)	$CoCl_2(CNC_2H_5)_2$	Green pleochroic crystals			27, 58
Dibromobis(phenylisocyano)-cobalt(II)	$CoBr_2(CNC_6H_5)_2$	Green powder		(7) 4.47	66
Tetrakis(methylisocyano)-cobalt(II) chloride	$[Co(CNCH_3)_4]Cl_2$	Violet crystals	115 (dec.)	(2) 1250 × 10^{-6} (5) 245	113
Tetrakis(methylisocyano)-cobalt(II) bromide	$[Co(CNCH_3)_4]Br_2$	Violet crystals	140 (dec.)	(2) 1230 × 10^{-6} (5) 242	113
Diiodotetrakis(methyliso-cyano)cobalt(II)	$CoI_2(CNCH_3)_4$	Olive green powder		(2) −180 × 10^{-6} (6) 1050 × 10^{-6}	113
		Brown crystals	250 (dec.)	(2) 1160 × 10^{-6} (5) 245	
Iododecakis(methylisocyano)-dicobalt(II) perchlorate	$[Co_2I(CNCH_3)_{10}](ClO_4)$	Dark brown crystals	222 (dec.)	(2) −82 × 10^{-6} (5) 370 (6) 1100 × 10^{-6}	113
Dichlorotetrakis(phenyliso-cyano)cobalt(II)	$CoCl_2(CNC_6H_5)_4$	Green needles		(7) 3.27	66
Dibromotetrakis(phenyliso-cyano)cobalt(II)	$CoBr_2(CNC_6H_5)_4$	Green needles		(7) 1.99	66

Diiodotetrakis(phenylisocyano)cobalt(II)	$CoI_2(CNC_6H_5)_4$	Dark green crystals with metallic reflectances	(2)	164×10^{-6}	66
			(8)	1372×10^{-6}	
		Black crystals	(2)	1440×10^{-6}	
Diiodotetrakis(*p*-tolylisocyano)cobalt(II)	$CoI_2(CNC_7H_7)_4$	Yellow-brown crystals	(2)	1425×10^{-6}	74
Diiodotetrakis(*p*-anisylisocyano)cobalt(II)	$CoI_2(CNC_7H_7O)_4$	Dark-green crystals	(2)	-168×10^{-6}	74
		Brown crystals	(2)	1475×10^{-6}	
			(3)	6.54	
			(9)	6.93	
Diiodotetrakis(*m*-chlorophenylisocyano)cobalt(II)	$CoI_2(CNC_6H_4Cl)_4$	Yellow-brown crystals	(2)	1380×10^{-6}	74
Diiodotetrakis(*p*-chlorophenylisocyano)cobalt(II)	$CoI_2(CNC_6H_4Cl)_4$	Yellow-brown crystals	(2)	1487×10^{-6}	74
Diiodotetrakis(2,4-dimethylphenylisocyano)cobalt(II)	$CoI_2(CNC_8H_9)_4$	Yellow-brown crystals	(2)	1400×10^{-6}	74
Diiodotetrakis(3-chloro-2-methylphenylisocyano)-cobalt(II)	$CoI_2(CNC_7H_6Cl)_4$	Violet crystals	(2)	110×10^{-6}	74
		Yellow-brown crystals	(2)	1270×10^{-6}	
Diiodotetrakis(4-chloro-2-methylphenylisocyano)-cobalt(II)	$CoI_2(CNC_7H_6Cl)_4$	Yellow-brown crystals	(2)	1190×10^{-6}	74
Diiodotetrakis(2,5-dichloro phenylisocyano)cobalt(II)	$CoI_2(CNC_6H_3Cl_2)_4$	Dark crystals with green reflectances	(2)	-80×10^{-6}	74
		Brown crystals	(2)	1264×10^{-6}	74

(continued)

TABLE VII (*continued*)

Name	Formula	Color and crystal form	M.p. or dec. temp., °C.	Other data[a]	Ref.
Diiodotetrakis(β-naphthylisocyano)cobalt(II)	$CoI_2(CNC_{10}H_7)_4$	Blue powder Brown powder		(2) -30×10^{-6} (2) 1270×10^{-6}	74
Potassium dibromotetrakis(*p*-isocyanobenzensulfonate)-cobaltate(II)	$K_4[CoBr_2(CNC_6H_4SO_3)_4]$	Dark brown powder		(10) 1198×10^{-6}	105
Cobalt(II) dibromotetrakis(*p*-isocyanobenzoate)cobaltate(II)	$Co_2[CoBr_2(CNC_6H_4COO)_4]$	Brown substance		(10) 14025×10^{-6}	105
Cobalt(II) diiodotetrakis(*p*-isocyanobenzoate)cobaltate(II)	$Co_2[CoI_2(CNC_8H_4COO)_4]$	Dark blue substance		(10) 14020×10^{-6}	105
Bromopentakis(phenylisocyano)cobalt(II) perchlorate	$[CoBr(CNC_6H_5)_5]ClO_4$	Black crystals		(10) 90×10^{-6}	74
Iodopentakis(phenylisocyano)cobalt(II) perchlorate	$[CoI(CNC_6H_5)_5]ClO_4$	Black crystals		(10) 80×10^{-6}	74
Iodopentakis(*p*-tolylisocyano)cobalt(II) perchlorate	$[CoI(CNC_7H_7)_5]ClO_4$	Black crystals			74
Iodopentakis(*p*-anisylisocyano)cobalt(II) perchlorate	$[CoI(CNC_7H_7O)_5]ClO_4$	Black crystals		(5) 218 (10) 118×10^{-6}	74
Pentakis(methylisocyano)-cobalt(II) perchlorate	$[Co(CNCH_3)_5](ClO_4)_2$	Red crystalline powder Blue crystals	152 (dec.)	(2) -120×10^{-6} (6) 1260×10^{-6} (2) 1265×10^{-6}	113
Pentakis(phenylisocyano)-cobalt(II) perchlorate	$[Co(CNC_6H_5)_5](ClO_4)_2$	Green-blue needles		(2) 1270×10^{-6}	106

Pentakis(*o*-tolylisocyano)-cobalt(II) perchlorate	$[Co(CNC_7H_7)_5](ClO_4)_2$	Green needles	(2) 1293×10^{-6}	106
Pentakis(*p*-tolylisocyano)-cobalt(II) perchlorate	$[Co(CNC_7H_7)_5](ClO_4)_2$	Green needles	(2) 1286×10^{-6} (11) 23.2	106
Dibromotetrakis(phenylisocyano)cobalt(III) bromide	$[CoBr_2(CNC_6H_5)_4]Br$	Dark green prisms		104
Diiodotetrakis(*p*-tolylisocyano)cobalt(III) iodide	$[CoI_2(CNC_7H_7)_4]I$	Dark brown prisms		104
Diiodotetrakis(*p*-anisylisocyano)cobalt(III) iodide	$[CoI_2(CNC_7H_7O)_4]I$	Dark green prisms		104
Diiodotetrakis(2-chloro-6-methylphenylisocyano)-cobalt(III) perchlorate	$[CoI_2(CNC_7H_6Cl)_4]ClO_4$	Brown prisms		104
Diiodotetrakis(*p*-tolylisocyano)cobalt(III) perchlorate	$[CoI_2(CNC_7H_7)_4]ClO_4$	Dark brown prisms		104
Iodopentakis(*o*-tolylisocyano)cobalt(III) perchlorate	$[CoI(CNC_7H_7)_5](ClO_4)_2$	Brown prisms		104
Iodopentakis(*p*-tolylisocyano)cobalt(III) perchlorate	$[CoI(CNC_7H_7)_5](ClO_4)_2$	Dark brown prisms		104
Iodopentakis(benzylisocyano)-cobalt(III) perchlorate	$[CoI(CNC_7H_7)_5](ClO_4)_2$	Red-violet tablets		

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[a] (1) Dipole moment of $10^{-2}M$ benzene solution at 20°C. (2) Magnetic susceptibility of the solid at 20°C. (3) Conductivity of 1/5000*M* nitrobenzene solution at 19°C. (4) Conductivity of $10^{-3}M$ nitrobenzene solution at 19°C. (5) Conductivity of $10^{-3}M$ aqueous solution at 15°C. (6) Magnetic susceptibility of aqueous solution at 20°C. (7) Magnetic moment (uncorrected). (8) Magnetic susceptibility of methylene chloride solution (0.05 mole per liter) at 21°C. (9) Conductivity of $1.5 \times 10^{-3}M$ methylene chloride solution at 17°C. (10) Magnetic susceptibility of the solid at 18°C. (11) Conductivity of $0.92 \times 10^{-3}M$ nitrobenzene solution at 20°C.

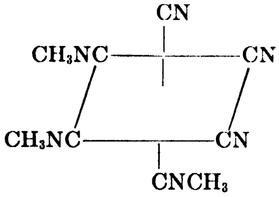
(III), (*b*) compounds obtained by reaction of isocyanides with cobalt(II) salts and related compounds, and (*c*) substitution compounds of cobalt nitrosylcarbonyl.

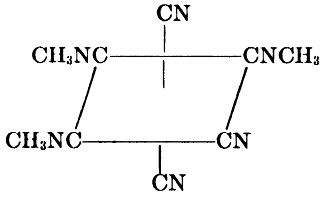
a. Compounds Obtained by Alkylation of Hexacyanocobaltates(III)

The alkylation reaction was carried out by Hartley (33) by gently warming a mixture of silver hexacyanocobaltate(III) and methyl iodide. The reaction can be written as follows:

$$Ag_3[Co(CN)_6] + 3\ CH_3I \longrightarrow (CH_3)_3Co(CN)_6 + 3\ AgI$$

The "methylcobalticyanide" thus obtained is a mixture of two isomeric forms, α and β, which can be separated owing to their different solubilities in water and alcohol. The solubility of the α form is 0.16% in water at 7° and 0.04% in boiling alcohol; the solubility of the β form is 0.44% in water at 7° and 1.4% in boiling alcohol. No interpretation of this isomerism is given by the author, but it is obvious that a tricyanotris(methylisocyano)cobalt(III) can exist in two isomeric forms:





Both the α and β forms of "methylcobalticyanide" give insoluble double salts with silver hexacyanocobaltate(III). The formation of these adducts as by-products in the alkylation reaction causes a considerable lowering in the yield of "methylcobalticyanide."

Hölzl and co-workers (54) studied the direct alkylation of hexacyanocobaltic(III) acid with alcohols. The reaction proceeds easily with methanol, with increasing difficulty with ethanol and propanol. Some of the intermediate products were isolated as pyridinium salts, e.g., $(Py)_3H_2[Co(CN)_4(CNCH_3)_2]$ and $(Py)_3H[Co(CN)_5(CNCH_3)]$. The presence of three pyridine molecules per two and one hydrogen atom, respectively, was not explained by Hölzl, who called them "anomalous salts."

Previously, the free acid $H_2[Co(CN)_5(CNC_2H_5)]$ had been obtained by Bolser and Richardson (4).

b. Compounds Obtained by Reaction of Isocyanides with Cobalt(II) Salts, and Related Compounds

A number of cobalt(II) salts, namely, the halides, the thiocyanate, and the perchlorate, react with isocyanides to give addition products of various and interesting types. Most of these compounds are remarkably stable, though less so than the isocyanide derivatives of cobalt(I), into which they can be converted easily by mild reduction. In some cases, e.g., with cobalt(II) acetate and nitrate, the reduction to cobalt(I) is spontaneous and immediate, so that the corresponding cobalt(II) compounds cannot be isolated. The isocyano derivatives of cobalt(III), which can be obtained by oxidation both of Co^{I} and Co^{II} compounds, are also stable and well defined substances.

Since the cobalt(II) derivatives, when stable, are the first to be obtained in the reaction between cobalt(II) salts and isocyanides, they will be dealt with first.

(1) Derivatives of Cobalt(II). Cobalt(II) halides form with isocyanides two series of compounds of composition corresponding to $CoX_2(CNR)_2$ and $CoX_2(CNR)_4$. The thiocyanate gives only compounds of the type $Co(SCN)_2(CNR)_2$ and the perchlorate compounds $Co(CNR)_5(ClO_4)_2$.

(a) Diisocyanide Derivatives. The compounds $CoCl_2(CNCH_3)_2$, $CoBr_2(CNCH_3)_2$, and $Co(SCN)_2(CNCH_3)_2$ (Sacco and Freni (111)) are green crystalline substances, readily soluble in water and methanol, sparingly soluble in organic solvents. They have a magnetic susceptibility which is the average between the values of the free Co^{2+} ion and of Co^{II} in its "inner complexes," and have been assigned the structure of tetrahalogeno- and tetrathiocyanocobaltates(II) of tetrakis(methylisocyano)cobalt(II): $[Co(CNCH_3)_4][CoX_4]$ ($X = Cl, Br, SCN$). The proposed structure is supported by measurements of electrical conductivity in aqueous solution, and by comparison between the UV spectra of these compounds in aqueous alcoholic solution and the spectra of the ions $[Co(CNR)_4]^{2+}$ and $[CoX_4]^{2-}$.

An analogous compound, $CoCl_2(CNC_2H_5)_2$, green crystalline powder soluble in water and alcohol, had been previously prepared by Hofmann and Bugge (58). The UV absorption spectra of its aqueous solutions (27) had shown that, unlike most addition compounds of this type, it is not decomposed by solvents. However, its structure has not been fully investigated.

The aryl derivative $CoBr_2(CNC_6H_5)_2$ is a green crystalline powder, insoluble in water and alcohol, and has a magnetic moment near to that of the free Co^{2+} ion (66). The compounds $Co(SCN)_2(CNAr)_2$ (Ar = phenyl, *p*-tolyl, *p*-anisyl) are green crystalline substances, practically insoluble in all solvents, and, like their methyl analogue, have magnetic moments intermediate between those of Co^{2+} and Co^{II} in inner complexes.

(*b*) *Tetraisocyanide derivatives.* The compounds $CoCl_2(CNCH_3)_4$ and $CoBr_2(CNCH_3)_4$ (113) are crystalline substances of blue-violet colors, soluble in water, alcohol, and nitrobenzene, very sparingly soluble in other organic solvents. The analogous phenyl derivatives, $CoCl_2(CNC_6H_5)_4$ and $CoBr_2(CNC_6H_5)_4$ (66), are sparingly soluble crystalline powders. They all have magnetic moments corresponding to one electron spin, with the exception of $CoCl_2(CNC_6H_5)_4$, which exhibits a much higher moment. These compounds might be formulated either as tetraisocyanocobalt(II) halides, $[Co(CNR)_4]X_2$, with a tetracoordinated cobalt atom using dsp^2 hybrid orbitals, or as dihalogenotetraisocyanocobalt(II) compounds, $CoX_2(CNR)_4$, with a hexacoordinated cobalt and d^2sp^3 orbitals. Conductivity measurements on the methylisocyanide derivatives in aqueous solution showed that these are electrolytes and therefore have to be assigned, at least in solution, the tetracoordinated square planar structure. No conductivity data are available for phenylisocyanide derivatives.

The isocyanide derivatives of cobalt(II) iodide, described by Malatesta and co-workers (66,74,78), are easily obtained in a pure state by simple addition of isocyanide to an alcoholic solution of cobalt iodide. They have compositions corresponding to $CoI_2(CNR)_4$, where R is alkyl or aryl, and exist in two different forms, called α and β. The compounds of the α-type are diamagnetic crystalline substances, of dark green color with metallic reflectance when in the form of large crystals, and blue-violet when finely powdered. They are moderately soluble in methylene chloride, chloroform, and nitrobenzene, giving intensely colored violet solutions, sparingly soluble in the other organic solvents, and insoluble in water. The methylisocyanide derivative is instead a light green crystalline powder, soluble in water, and insoluble in organic solvents (113).

The compounds of the β-type are yellow or brown crystalline powders, even less soluble than the corresponding α-forms, and have magnetic susceptibilities corresponding to one unpaired electron.

As the only possible transition in the solid state is $\alpha \rightarrow \beta$, it may be concluded that the β-form is the stable one. This suggestion is supported by the fact that the α-forms, when they can be obtained, are always the first to separate from the solutions. The α-forms can be transformed into the β by prolonged warming at 40–60°, or more rapidly by boiling in presence of a solvent in which they are only slightly soluble, e.g., alcohol or acetone. The β-forms, on the other hand, are reconverted into the α by dissolution and reprecipitation from cold solutions. In some cases a partial $\beta \rightarrow \alpha$ transformation is obtained by finely grinding the β-form. In solution, an equilibrium $\alpha \rightleftharpoons \beta$ is established, which may lie more on one side or on the other depending on the solvent and the concentration. Its position can be roughly estimated from the magnetism of the solution. An increase in the concentration always shifts the equilibrium toward the α-form, as may be seen from the fact that the color of the solution turns from yellow-brown (β-form) to violet (α-form) on concentration.

For the compounds containing aryl isocyanides, the stability of the α-form depends very much on the groups attached to the benzene ring; in some cases the α-form may even become too unstable to be isolated. However, no indication of the reasons for this influence could be inferred from the study of a number of different arylisocyanide derivatives, nor could any regularity be detected. The paramagnetism of the β-forms has the value expected for an inner complex of cobalt(II). On the basis of conductivity measurements in dilute solutions, and by analogy with the corresponding chloro and bromo compounds, the β-forms are to be considered the tetraisocyanocobalt(II) iodides, $[Co(CNR)_4]I_2$. The diamagnetism of the α-forms might be ascribed either to a resonance of the type $Co^{I} \longleftrightarrow Co^{III}$ or to spin pairing between pairs of cobalt(II) atoms. Only an X-ray investigation will make possible an unambiguous assignment of the structure of the α-form. At the moment there are only indirect suggestions, the most substantial of which seems to be the comparison between the α-$CoI_2(CNC_6H_5)_4$ and the analogous diamagnetic rhodium compound, $RhI_2(CNC_6H_5)_4$ (115). In fact, the rhodium compound, for which a dimeric structure, $[Rh_2I_2(CNC_6H_5)_8]I_2$, has been proved on the basis of chemical behavior, has color and appearance identical with the cobalt derivative, and the two compounds have been shown to be isomorphous by comparison of their X-ray powder patterns.

The methylisocyanide derivative, $CoI_2(CNCH_3)_4$ (113), when treated with sodium perchlorate in aqueous solution, gives a compound of composition $Co_2(CNCH_3)_{10}I(ClO_4)_3$, diamagnetic in the solid state, paramagnetic in solution, with a magnetic moment corresponding to one unpaired electron per cobalt atom. To account for the conductivity of its aqueous solutions, this compound was assigned the structure of μ-iododecakis(methylisocyano)cobalt(II) perchlorate, $[(CH_3NC)_5CoICo(CNCH_3)_5](ClO_4)_3$. The aryl derivatives, $CoI_2(CNAr)_4$, do not react with sodium perchlorate in chloroform–alcohol solution (74). With the amount of silver perchlorate exactly calculated to substitute one iodine atom, in chloroform–benzene solution, they give a rather complicated reaction:

$$5\,CoI_2(CNAr)_4 + 4\,AgClO_4 \longrightarrow 4\,[CoI(CNAr)_5](ClO_4) + 4\,AgI + CoI_2$$

The bromides, $[Co(CNAr)_4]Br_2$, react in an analogous way. The compounds $[CoX(CNAr)_5](ClO_4)$ (X = Br, I) are black-violet crystalline substances, which in nitrobenzene solution behave as strong uni-univalent electrolytes. In the solid state they are diamagnetic; no data are available for the magnetic susceptibility of the solutions.

The existence of the cation $[CoX(CNAr)_5]^+$ (X = Br, I) (74) shows that $[Co(CNAr)_5]^{2+}$, though saturated with respect to isocyanides, is not coordinatively saturated in the strict sense, as it is able to bind a halogen ion.

The diamagnetism of the compounds $[CoX(CNAr)_5](ClO_4)$, even if limited to the solid state, is rather difficult to explain. In fact, since the cobalt atoms are coordinatively saturated, it seems difficult to think of a structure where the metal–metal distance would allow spin coupling.

(c) *Pentaisocyanide derivatives.* The addition products of alkyl and aryl isocyanides with cobalt perchlorate, of composition $Co(CNR)_5(ClO_4)_2$ (106), are the only sure examples of pentacoordinated complex cations of cobalt(II).

The methylisocyanide derivative, $Co(CNCH_3)_5(ClO_4)_2$, has been very recently obtained by Sacco and Freni (113) in two forms. Both are soluble in water and alcohol. One is light blue and paramagnetic (one electron spin), the other red and diamagnetic. While in the solid state the latter seems to be the stable one, the solutions are always paramagnetic and have electric conductivity corresponding to a formula of pentakis(methylisocyano)cobalt(II) perchlorate,

$[Co(CNCH_3)_5](ClO_4)_2$. The diamagnetism of the red form is due evidently to the crystal structure.

The aryl derivatives, $[Co(CNAr)_5](ClO_4)_2$ (Ar = phenyl, *p*-tolyl, *p*-anisyl), exist only in the paramagnetic form (one unpaired electron). They are green crystalline substances, soluble in methylene chloride and chloroform, sparingly soluble in alcohol and ether, and insoluble in water.

(2) Derivatives of Cobalt(I). These very interesting compounds were missed by the chemists who, like K. A. Hofmann, first investigated the reaction between isocyanides and cobalt(II) salts. Yet, as later shown by Malatesta and co-workers (72,77), they are very stable and easy to obtain, being formed whenever a cobalt(II) salt is heated in alcoholic solution with an excess of isocyanide.

These compounds are crystalline substances, of colors varying from yellow to brown, with composition corresponding to $Co(CNR)_5X$, where X is a univalent anion. They are quite stable to air, soluble in most organic solvents, and insoluble in water. In solution they have the character of strong uni-univalent electrolytes. The corresponding hydroxides, $[Co(CNR)_5]OH$, are stable in absence of carbon dioxide and have a strong alkaline reaction. As expected for derivatives of cobalt(I), these compounds are diamagnetic. The cation $[(Co(CNR)_5]^+$, by analogy with the isoelectronic molecule $Fe(CO)_5$, may be considered to have a trigonal bipyramidal structure.

The most suitable way to prepare the salts of pentaisocyanocobalt(I) is a mild reduction of the divalent derivatives $[Co(CNR)_5]$-$(ClO_4)_2$ and $Co(CNR)_4I_2$. The pentaisocyanocobalt(II) perchlorates can be reduced by simply boiling them in alcohol in presence of isocyanide. With hydrazine the reaction takes place immediately in the cold:

$$4\,Co(CNR)_5(ClO_4)_2 + N_2H_4 \longrightarrow 4\,Co(CNR)_5ClO_4 + 4\,HClO_4 + N_2$$

The tetraisocyanocobalt(II) iodides require a mild reducing agent, such as dithionite, hydrazine acetate, or metals. With hydrazine the reaction proceeds as follows:

$$5\,Co(CNR)_4I_2 + N_2H_4 \longrightarrow 4\,Co(CNR)_5I + CoI_2 + 4\,HI + N_2$$

With metals the reaction is analogous but, when silver or mercury is used, the final product is an adduct between the pentaisocyanocobalt(I) salt and the silver or mercury salt:

$$5\,Co(CNR)_4I_2 + 4\,Ag \longrightarrow 4\,Co(CNR)_5I\cdot AgI + CoI_2$$
$$5\,Co(CNR)_4I_2 + 2\,Hg \longrightarrow 2\{Co(CNR)_5I\}_2\cdot HgI_2 + CoI_2$$

The addition compounds between the halides of pentaisocyanocobalt(I) and the halides of heavy metals can be formulated as halometallates of the cation $[Co(CNR)_5]^+$, e.g., $[Co(CNR)_5]_2[HgI_4]$, but it is difficult to formulate in a similar way the analogous addition compounds of $[Co(CNR)_5](ClO_4)$.

The pentakis(arylisocyano)cobalt(I) cations are formed also by treating dicobalt octacarbonyl with isocyanides. Hieber and Böckly were the first to investigate this reaction (40). They attributed to the methylisocyanide derivative the formula $[Co(CO)(CNCH_3)_3]_2$ and to the arylisocyanide derivatives the formula $Co_2(CO)_3(CNR)_5$. These formulations were, however, shown to be incorrect. In fact, Sacco found (103) that the products, when pure, have composition corresponding to $Co_2(CO)_4(CNR)_5$ and, because of their electrical conductivity in solution, must be formulated as the tetracarbonylcobaltates of pentaisocyanocobalt $[(Co(CNR)_5][Co(CO)_4]$.

This structure, later accepted by Hieber (43), was confirmed by preparing the same compounds in another way:

$$Na[Co(CO)_4] + [Co(CNR)_5](ClO_4) \longrightarrow [Co(CNR)_5][Co(CO)_4] + NaClO_4$$

The reaction between the dimeric cobalt carbonyl and isocyanides may therefore be written as follows:

$$[Co_2(CO)_8] + 5\,CNR \longrightarrow [Co(CNR)_5][Co(CO)_4] + 4\,CO$$

The compound $[Co(CNR)_5][Co(CO)_4]$, which contains one cobalt atom in the $+1$ oxidation state and the other in the -1 oxidation state, can be compared with the product formed by action of ethylenediamine (Ed) on iron pentacarbonyl, which has the composition $Fe_2(Ed)_3(CO)_4$ (38), and has to be formulated as the tetracarbonylferrate(-2) of tris(ethylenediamino)iron($+2$), $[Fe(Ed)_3][Fe(CO)_4]$ (42).

The reaction between aryl isocyanides and cobalt carbonyl is indicative of the different abilities of CO and CNR to stabilize the low valent states of the metals. Both ligands, however, tend to give ions where the metal orbitals are completely filled; actually, both the pentacoordinated Co($+1$) and the tetracoordinated Co(-1) have the E.A.N. of krypton.

(3) *Derivatives of Cobalt(III).* Three types of isocyanide deriva-

tives of cobalt(III) have been obtained by reaction of the isocyanide derivatives of cobalt(I) and cobalt(II) with oxidizing agents, such as bromine, iodine, hydrogen peroxide, nitrous acid, and amyl nitrite (104):

(*a*) The bromides of dibromotetrakis(arylisocyano)cobalt(III), $[CoBr_2(CNR)_4]Br$, and the analogous iodo derivatives are well-crystallized substances, soluble in chloroform and methylene chloride, and insoluble in alcohol. The bromo derivatives have a green, and the iodo compounds a dark brown, color. These compounds were obtained from the corresponding divalent halides with the required amount of halogen.

(*b*) The perchlorates of diiodotetrakis(arylisocyano)cobalt(III), $[CoI_2(CNR)_4](ClO_4)$, are dark brown crystalline substances, soluble in chloroform with violet color. They are obtained either by treating the diiodotetrakis(arylisocyano)cobalt(II) compounds with amyl nitrite or hydrogen peroxide, in presence of perchloric acid, or by addition of the calculated amount of iodine to the perchlorates of pentakis(arylisocyano)cobalt(I). It is interesting to notice that diiodotetrakis(benzylisocyano)cobalt(II), when oxidized with amyl nitrite or hydrogen peroxide, gives instead a compound of type (*c*).

(*c*) The perchlorates of iodopentakis(arylisocyano)cobalt(III), $[CoI(CNR)_5](ClO_4)_2$, are brown-red crystalline substances, soluble in chloroform, insoluble in alcohol. They were prepared from the corresponding perchlorates of pentakis(arylisocyano)cobalt(II), on addition of the calculated amount of iodine in methylene chloride.

Compounds of the type $[Co(CNR)_6]X_3$ could not be obtained, so that the presence of at least one anionic ligand appears to be essential to the stability of the isocyanide compounds of trivalent cobalt.

c. Substitution Compounds of Cobalt Nitrosylcarbonyl

The reaction between $Co(NO)(CO)_3$ and aryl isocyanides takes place rapidly and neatly in alcoholic solution, yielding the nitrosylcarbonyldiisocyanocobalt compounds (73):

$$[Co(NO)(CO)_3] + 2\,CNR \longrightarrow [Co(NO)(CO)(CNR)_2] + 2\,CO$$

Compounds of complete substitutions could not be obtained in this way, but were suitably prepared by treating with isocyanides the black form of nitrosylpentaamminocobalt(II) chloride, in presence of hydrazine (73):

$$2\,[Co(NO)(NH_3)_5]Cl_2 + 6\,CNR + N_2H_4 \longrightarrow 2\,Co(NO)(CNR)_3 + N_2 + 6\,NH_3 + 4\,NH_4Cl$$

The nitrosyltriisocyanocobalt compounds can also be prepared by reacting the pentaisocyanocobalt(I) salts with hydroxylamine, in alcoholic solution containing ammonia (71,73). The reaction, analogous to that of iron, may be written as follows:

$$2\,NH_2OH \longrightarrow NH_3 + NOH + H_2O$$

$$[Co(CNR)_5]^+ + NOH + NH_3 \longrightarrow Co(NO)(CNR)_3 + NH_4^+ + 2\,CNR$$

The nitrosylcarbonylbis(arylisocyano)cobalt and nitrosyltris(arylisocyano)cobalt compounds are orange-red crystalline substances, soluble in most organic solvents, quite stable to air. They are all diamagnetic. The nitrosyltris(arylisocyano) compounds have rather high dipole moments in benzene solution.

2. Rhodium

a. Derivatives of Rhodium(I)

Rhodium(III) chloride and the other soluble salts and complexes of rhodium(III) do not react with isocyanides in the cold. However, when a solution of rhodium(III) chloride in ethanol is refluxed with an excess of isocyanide, a lively reaction occurs and through many undetermined steps, shown by formation of amorphous precipitates of various colors, a stable blue-violet solution is obtained (85). On addition of bulky anions, such as ClO_4^- and $[PF_6]^-$, well-crystallized and intensely colored substances separate from this solution. They are diamagnetic and behave as strong uni-univalent electrolytes. According to their analyses they can be formulated as the salts of tetrakis(arylisocyano)rhodium(I), $[Rh(CNR)_4]X$, where X is a univalent anion.

The formation reactions are presumed to be:

$$RhCl_3 + 4\,CNR \longrightarrow [RhCl_2(CNR)_4]Cl$$

$$[RhCl_2(CNR)_4]Cl + CNR + H_2O \longrightarrow [Rh(CNR)_4]Cl + RNCO + 2\,HCl$$

$$[Rh(CNR)_4]Cl + NaClO_4 \longrightarrow [Rh(CNR)_4]ClO_4 + NaCl$$

TABLE VIII
Isocyanide Compounds of Rhodium

Name	Formula	Color and crystal form	M.p. or dec. temp., °C.	Other data[a]	Ref.
Chlorocarbonylbis(*p*-anisylisocyano)rhodium(I)	$RhCl(CO)(CNC_7H_7O)_2$	Ivory white needles	140–50 (dec.)		116
Bromocarbonylbis(*p*-anisylisocyano)rhodium(I)	$RhBr(CO)(CNC_7H_7O)_2$	Pale yellow needles	165–70		116
Tetrakis(phenylisocyano)rhodium(I) perchlorate	$[Rh(CNC_6H_5)_4]ClO_4$	Yellow prisms (from benzene)	172–80		
Tetrakis(*p*-tolylisocyano)rhodium(I) perchlorate	$[Rh(CNC_7H_7)_4]ClO_4$	Yellow tablets (from benzene)	198 (dec.)	(1) -50×10^{-6} (2) 30	85
		Violet needles (from ethanol)	207 (dec.)	(1) -60×10^{-6} (2) 31	
		Blue needles (from methanol)	200 (dec.)	(1) -80×10^{-6} (2) 31	85
Tetrakis(*p*-anisylisocyano)rhodium(I) perchlorate	$[Rh(CNC_7H_7O)_4]ClO_4$	Green needles	180 (dec.)	(2) 30	
Tetrakis(*p*-anisylisocyano)rhodium(I) hexafluorophosphate	$[Rh(CNC_7H_7O)_4]PF_6$	Green leaflets (from benzene)	230 (dec.)	(1) -90×10^{-6} (2) 28	85
		Bright red needles (from aqueous ethanol)	215 (dec.)	(1) -70×10^{-6}	
		Violet tablets (from chloroform)	237 (dec.)	(1) -60×10^{-6}	

(continued)

TABLE VIII (*continued*)

Name	Formula	Color and crystal form	M.p. or dec. temp., °C.	Other data[a]	Ref.
Tetrakis(*p*-chlorophenylisocyano)rhodium(I) chloride	$[Rh(CNC_6H_4Cl)_4]Cl$	Blue hair-like needles (from methanol)	140 (dec.)	(1) -50×10^{-6}	85
		Violet prisms (from ethanol)	137 (dec.)	(1) -135×10^{-6}	
Bis(phenylisocyano)bis(triphenylphosphine)rhodium(I) chloride	$[Rh(CNC_6H_5)_2\{(C_6H_5)_3P\}_2]Cl$	Yellow prisms	165–70 (dec.)		116
Bis(phenylisocyano)bis(triphenylphosphine)rhodium(I) bromide	$[Rh(CNC_6H_5)_2\{(C_6H_5)_3P\}_2]Br$	Yellow prisms	180–5 (dec.)		116
Bis(phenylisocyano)bis(triphenylphosphine)rhodium(I) iodide	$[Rh(CNC_6H_5)_2\{(C_6H_5)_3P\}_2]I$	Yellow-brown prisms	180–5 (dec.)		116
Bis(*p*-anisylisocyano)bis(triphenylphosphine)rhodium(I) chloride	$[Rh(CNC_7H_7O)_2\{C_6H_5)_3P\}_2]Cl$	Yellow needles	140–5 (dec.)	(3) 19.0	116
Bis(*p*-anisylisocyano(bis(triphenylphosphine)rhodium(I) iodide	$[Rh(CNC_7H_7O)_2\{(C_6H_5)_3P\}_2]I$	Orange needles	155–60 (dec.)	(3) 18.8	116
Bis(*p*-anisylisocyano)bis(triphenylphosphine)rhodium(I) perchlorate	$[Rh(CNC_7H_7O)_2\{(C_6H_5)_3P\}_2]ClO_4$	Yellow prisms	180 (dec.)	(3) 20.1	116
Bis(*p*-anisylisocyano)bis(triphenylarsine)rhodium(I) perchlorate	$[Rh(CNC_7H_7O)_2\{(C_6H_5)_3As\}_2]ClO_4$	Yellow-orange prisms	185–90 (dec.)	(3) 19.8	116

Bis(*p*-anisylisocyano)bis-(triphenylstibine)-rhodium(I) perchlorate	$[Rh(CNC_7H_7O)_2\{(C_6H_5)_3Sb\}_2]ClO_4$	Yellow prisms	180–90 (dec.)	(3)	21.0	116
Bis(*p*-anisylisocyano)bis-(triphenylphosphite)-rhodium(I) perchlorate	$[Rh(CNC_7H_7O)_2\{(C_6H_5O)_3P\}_2]ClO_4$	Yellow prisms	157–60 (dec.)	(3)	23.9	116
Diiodooctakis(phenyliso-cyano)dirhodium(II) iodide	$[Rh_2I_2(CNC_6H_5)_8]I_2$	Dark crystals with green reflectances	140–5 (dec.)			115
Diiodooctakis(phenyliso-cyano)dirhodium(II) perchlorate	$[Rh_2I_2(CNC_6H_5)_8](ClO_4)_2$	Dark leaflets with metallic reflectances	210–5			115
Triiodoheptakis(phenyliso-cyano)dirhodium(II) tetraphenylborate	$[Rh_2I_3(CNC_6H_5)_7][(C_6H_5)_4B]$	Deep red needles	141–2			115
Triiodoheptakis(phenyliso-cyano)dirhodium(II) triiodide	$[Rh_2I_3(CNC_6H_5)_7]I_3$	Deep red needles with green reflectances	130–5 (dec.)			115
Dichlorotetrakis(phenyl-isocyano)rhodium(III) chloride	$[RhCl_2(CNC_6H_5)_4]Cl$	Blue-violet prisms	140–5 (dec.)			115
Dichlorotetrakis(phenyl-isocyano)rhodium(III) perchlorate	$[RhCl_2(CNC_6H_5)_4]ClO_4$	Olive green hair-like needles	210–5 (dec.)			115

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[a] (1) Magnetic susceptibility of the solid. (2) Molar conductivity in nitrobenzene at infinite dilution. (3) Molar conductivity in 1/1000*M* nitrobenzene solution.

This is partially confirmed by the isolation of the intermediate trivalent product, $[RhCl_2(CNC_6H_5)_4]Cl$.

The salts of tetrakis(arylisocyano)rhodium(I) give stable solvates of different colors and crystal forms with various solvents. This tendency to solvation is quite unusual among the isocyanide complexes and may be explained by assuming that in this case the vacant $5p_z$ orbital of the tetracoordinated rhodium(I) is able to accept a lone electron pair from a suitable donor molecule. This simple dative bond is much weaker than the isocyanide–metal bonds, and the substitution, as well as the removal, of the molecule of solvent is quite easy. The unsolvated salts can be obtained from benzene, ethyl acetate, and alcohols higher than propanol, and are yellow or green; the colors of the solvates vary with the solvent, the anion, and the isocyanide. Such an explanation, however, does not account for the fact that in some cases two or even more forms, of different colors but having nearly identical composition, have been obtained for the same solvate.

The salts of tetrakis(arylisocyano)rhodium(I) can also be prepared from rhodium carbonyl halides and isocyanides. This method is the more suitable for the preparation of the derivatives of phenyl isocyanide, which by the other way are obtained only in very poor yields. When *p*-anisyl isocyanide is used, the partially substituted intermediate products can be isolated (116):

$$Rh_2Cl_2(CO)_4 + 4\,CNR \longrightarrow 2\,RhCl(CO)(CNR)_2 + 2\,CO$$

$$RhCl(CO)(CNR)_2 + 2\,CNR \longrightarrow [Rh(CNR)_4]Cl + CO$$

The chlorocarbonylbis(*p*-anisylisocyano)rhodium(I) and the analogous bromo compound are pale yellow crystalline substances, soluble in chloroform with red-violet color. They are nonelectrolytes and monomeric in solution. With triphenylphosphine they react giving tetracoordinated salts of rhodium(I) (116):

$$RhCl(CO)(CNR)_2 + 2\,PR_3 \longrightarrow [Rh(CNR)_2(PR_3)_2]Cl + CO$$

An analogous reaction occurs with triarylarsines, triarylstibines, and the esters of phosphorous acid. These mixed salts are yellow or orange-yellow crystalline substances, soluble in most organic solvents. Unlike the tetraisocyanide salts, they have no tendency to form solvates.

b. Compounds of Rhodium(II) and Rhodium(III) with Phenyl Isocyanide

It has already been mentioned that the behavior of phenyl isocyanide toward rhodium(III) chloride is somewhat different from that of the other aryl isocyanides. In fact, the blue-violet solution obtained by refluxing phenyl isocyanide and rhodium(III) chloride, under the conditions that usually lead to the univalent tetracoordinated salts, yields instead a derivative of trivalent rhodium (115). This is a diamagnetic, blue-violet crystalline product, which from its analysis and conductivity can be formulated as the chloride of dichlorotetrakis(phenylisocyano)rhodium(III), $[RhCl_2(CNC_6H_5)_4]Cl$. This formulation is confirmed by the formation of the corresponding perchlorate, $[RhCl_2(CNC_6H_5)_4]ClO_4$, on exchange with sodium perchlorate in alcoholic solution. When heated in ethanol in presence of a slight excess of phenyl isocyanide, this derivative of trivalent rhodium dissolves, giving a red-violet solution from which, on addition of sodium iodide, a dark crystalline product with green reflectances separates (115). This is a salt-like substance, of analysis corresponding to $RhI_2(CNC_6H_5)_4$. It is diamagnetic both in the solid state and in solution and is strictly similar to the α-form of the corresponding compounds of cobalt(II) (see page 351), with which it is shown to be isomorphous by comparison of the X-ray powder patterns.

On treating with sodium perchlorate in ethanol, the compound $RhI_2(CNC_6H_5)_4$ gives a dark crystalline substance that can be formulated as the perchlorate of diiodooctakis(phenylisocyano)dirhodium(II), $[Rh_2I_2(CNC_6H_5)_8](ClO_4)_2$. This shows that in the iodo compound one of the iodine atoms acts as ligand and suggests that the compound is the iodide of diiodooctakis(phenylisocyano)dirhodium(II), $[Rh_2I_2(CNC_6H_5)_8]I_2$. On the other hand, when treated with sodium tetraphenylborate in solution of methylene chloride and alcohol, the iodo compound gives a salt of formula $[Rh_2I_3(CNC_6H_5)_7][B(C_6H_5)_4]$ and a similar product, $[Rh_2I_3(CNC_6H_5)_7]I_3$, is obtained on reaction with iodine in chloroform solution in the molar ratio 1:1. These facts show that in solutions of chloroform and methylene chloride the equilibrium:

$$[Rh_2I_2(CNC_6H_5)_8]I_2 \rightleftharpoons [Rh_2I_3(CNC_6H_5)_7]I + CNC_6H_5$$

is present, which is shifted to the right in presence of anions capable of forming insoluble salts with univalent cations.

C. NICKEL, PALLADIUM, AND PLATINUM

Very few analogies can be observed among the isocyanide compounds of these elements.

In the divalent state they all form derivatives of the type $MeX_2 \cdot 2CNR$; but, while the nickel compounds are ill defined and unstable, those of palladium and platinum are extremely stable and well characterized. Besides, palladium compounds exist only in the monomeric nonionic form, $PdX_2(CNR)_2$, while those of platinum have been obtained both as $[Pt(CNR)_4][PtX_4]$ and $PtX_2(CNR)_2$.

In the zero valent state nickel forms tetracoordinated compounds, $Ni(CNR)_4$, soluble in organic solvents, whereas palladium gives dicoordinated insoluble compounds $Pd(CNR)_2$. No derivatives of platinum(0) have so far been described.

1. Nickel

a. Derivatives of Nickel(II)

A lively and very exothermic reaction occurs on addition of isocyanides to an alcoholic solution of nickel salts, which shows that the affinity of isocyanides toward Ni^{2+} ion is quite strong. Nevertheless, none of the products obtained by reacting nickel chloride and nickel cyanide with isocyanides is a stable and well-defined substance. They are brown powders that cannot be recrystallized and on heating do not melt sharply but gradually decompose into a black molten mass. Their composition corresponds to the formulas $NiCl_2(CNR)_2$, $Ni(CN)_2(CNR)_2$, and $Ni(CN)_2(CNR)_4$, and they were considered to be the isocyanide complexes of divalent nickel (65).

However, their lack of definite properties, together with the observation that they act as catalysts in the polymerization of free isocyanides, makes such a formulation rather doubtful. In fact, their analyses could correspond to the above formula even in the case they were not definite compounds but coprecipitated mixtures of nickel salts and solid polymers of isocyanides, because in most cases they were prepared by mixing the calculated amounts of reagents.

It may be remarked here that the metals which form halogenocarbonyls, such as $FeX_2(CO)_4$, $[PdCl_2(CO)]_2$, and $PtCl_2(CO)_2$, form also halogenoisocyano compounds. These may or may not be of a type similar to the corresponding halogenocarbonyl, e.g., $FeX_2(CNR)_4$,

TABLE IX
Isocyanide Compounds of Nickel

Name	Formula	Color and crystal form	M.p. or dec. temp., °C.	Ref.
Carbonyltris(methylisocyano)nickel(0)	$Ni(CO)(CNCH_3)_3$	Pale yellow crystals	110 (dec.)	40
Tetrakis(methylisocyano)nickel(0)	$Ni(CNCH_3)_4$	Pale yellow crystals		67
Tetrakis(phenylisocyano)nickel(0)	$Ni(CNC_6H_5)_4$	Canary yellow, very long needles	202–4 (dec.)	40, 62
Tetrakis(*p*-tolylisocyano)nickel(0)	$Ni(CNC_7H_7)_4$	Yellow needles		63, 67
Tetrakis(*p*-ethoxyphenylisocyano)nickel(0)	$Ni(CNC_8H_9O)_4$	Pale yellow fine needles	206–8 (dec.)	62
Tetrakis(β-naphthylisocyano)nickel(0)	$Ni(CNC_{10}H_7)_4$	Yellow-red needles		67

$PdX_2(CNR)_2$, $PtX_2(CNR)_2$, and $[Pt(CNR)_4][PtX_4]$, but are always very stable. The elements that, like nickel, chromium, molybdenum, and tungsten, do not form carbonyl halides, give instead very unstable and ill-defined isocyanide compounds in oxidation states other than zero. This consideration may account for the fact that no stable salts of the cation $[Ni(CNR)_4]^{2+}$ are known.

b. Derivatives of Nickel(0)

The isocyanide derivatives of nickel(0), of formula $Ni(CNR)_4$, are among the most interesting isocyanide compounds because of their great stability and ease of formation.

It may be interesting to recall that they were the first products of complete substitution of a metal carbonyl to be obtained, since only partially substituted compounds were previously known. Afterward it was found that many other ligands, all of the type with strong double bonding character, are able to give completely substituted carbonyl-like compounds. A number of derivatives of trivalent phosphorus, namely, PCl_3 (59), PF_3(117), $PCl_2C_6H_5$ (80), $PCl_2OC_6H_5$ (80), PCl_2CH_3 (100), form compounds of the type NiL_4, either by direct substitution from $Ni(CO)_4$ or in other ways. For instance the dichloromethylphosphine, PCl_2CH_3, reacts with metallic nickel, analogously to carbon monoxide itself (100):

$$Ni + 4\,PCl_2CH_3 \longrightarrow Ni(PCl_2CH_3)_4$$

The tetrakis(arylisocyano)nickels were obtained independently and almost at the same time (1947) by Hieber (39,40) and by Klages and Mönkemeyer (61,62), on reaction of aryl isocyanides with nickel tetracarbonyl:

$$Ni(CO)_4 + 4\,CNR \longrightarrow Ni(CNR)_4 + 4\,CO$$

The reaction takes place under mild conditions and yields only the tetrasubstituted products. This is most remarkable because nickel carbonyl is the only pure carbonyl from which it is possible to prepare completely substituted zero valent isocyanide compounds.

The other pure carbonyls either give a partial substitution, e.g., $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, and $Fe(CO)_5$, or disproportionate like $CO_2(CO)_8$. From $Ni(CO)_4$, no carbonylarylisocyanide derivatives could be obtained even if a defect of isocyanide was used, which can be ascribed either to a higher reactivity of the partially substituted products with respect to the pure carbonyl, or to disproportionation reactions of the type:

$$2\,Ni(CO)_2(CNR)_2 \longrightarrow Ni(CO)_4 + Ni(CNR)_4$$

Subsequently, the tetrakis(arylisocyano)nickels were prepared by Malatesta and Sacco (67) from nickel(II) compounds and isocyanides. The first positive results were obtained by reacting the bis(dimethylglyoximato)nickel(II) with aryl isocyanides in presence of hydrazine. The bis(dimethylglyoximato)nickel(II) was chosen as starting material because it was known that under high pressure of carbon monoxide it disproportionates to $Ni(CO)_4$ and a dimethylglyoxime (DGH_2) derivative of Ni^{IV} (41). An analogous disproportionation reaction could be expected to take place in presence of isocyanides; the addition of hydrazine had the purpose of reducing the Ni^{IV} as soon as it would form. In fact, the reaction proceeded according to the equation:

$$2\,Ni(DGH)_2 + 8\,CNR + N_2H_4 \longrightarrow 2\,Ni(CNR)_4 + 4\,DGH_2 + N_2$$

It was later seen that in presence of hydrazine all nickel salts undergo an analogous reaction, provided the medium is alkaline, and that even the presence of hydrazine is not strictly necessary, since the tetrakis(arylisocyano)nickels are formed slowly also from an alcoholic suspension of nickel hydroxide and an excess of aryl isocyanides. The reaction can be considered to be:

$$Ni(OH)_2 + 5\,CNR \longrightarrow Ni(CNR)_4 + RNCO + H_2O$$

The tetrakis(arylisocyano)nickel compounds are yellow crystalline substances, of moderate thermal stability, soluble in organic solvents. They are stable to air in the solid state, but decompose rapidly in solution. In absence of air, however, the solutions are quite stable and the products can be recovered unaltered (62). The tetrakis(arylisocyano)nickels are hydrophobic and are not affected by aqueous solutions of strong mineral acids and bases. Even aqueous potassium cyanide and the mixture of potassium cyanide and hydroxylamine, which attack all the other nickel complexes, are without effect on the tetraisocyanonickel compounds. On the other hand, they are completely destroyed by fuming nitric acid and by bromine.

Unlike aryl isocyanides, alkyl isocyanides do not completely displace carbon monoxide from $Ni(CO)_4$. The reaction between

$Ni(CO)_4$ and methyl isocyanide yielded a yellow crystalline product, which was formulated as the carbonyltris(methylisocyano)nickel(0), $Ni(CO)(CNCH_3)_3$ (40). This compound is remarkably stable. The residual molecule of carbon monoxide is very difficultly removed; it can be displaced slowly by a solution of iodine in pyridine, rapidly and quantitatively by heating with aryl isocyanides. The general properties of $Ni(CO)(CNCH_3)_3$ are similar to those of the tetraisocyanide compounds.

2. Palladium

a. Derivatives of Palladium(II)

Palladium halides react readily with aryl isocyanides, yielding stable and well-defined products which analyze as $PdX_2.2CNR$ (X = halogen atom) (1). They are orange crystalline substances, with generally high melting points, soluble in methylene chloride, chloroform, benzene, and nitrobenzene, very sparingly soluble in alcohol and ether. They are diamagnetic, nonelectrolytes, and monomeric in solution, and must therefore be formulated as dihalogenobis(arylisocyano)palladium(II) compounds, $PdX_2(CNR)_2$.

These compounds may be assigned a square planar structure with dsp^2 hybrid orbitals. It cannot be said whether the crystalline products that have been described have a *cis* or a *trans* configuration, but measurements of dipole moments in benzene seem to indicate that in this solvent the *cis* form, or at least an equilibrium where the *cis* form prevails, is present (1).

No isocyanide derivatives of the palladium(II) salts with noncoordinating anions could be prepared, which shows that neither the dicoordinated $[Pd(CNR)_2]^{2+}$ nor the tetracoordinated $[Pd(CNR)_4]^{2+}$ is stable. The instability of the latter cation may account for the fact that the compounds $PdX_2(CNR)_2$, unlike the analogous Pt(II) derivatives, exist only in the nonelectrolyte, monomeric form.

b. Derivatives of Palladium(0)

The aryl isocyanide derivatives of palladium(0), of composition corresponding to $Pd(CNR)_2$, are the first known examples of isocyanide compounds of a zero valent metal, of which the corresponding

TABLE X
Isocyanide Compounds of Palladium

Name	Formula	Color and crystal form	M.p. or dec. temp., °C.	Ref.
Bis(phenylisocyano)palladium(0)	$Pd(CNC_6H_5)_2$	Dark brown leaflets	170–90 (dec.)	81
Bis(*p*-tolylisocyano)palladium(0)	$Pd(CNC_7H_7)_2$	Dark brown leaflets	150–60 (dec.)	81
Bis(*p*-anisylisocyano)palladium(0)	$Pd(CNC_7H_7O)_2$	Dark brown leaflets	160–70 (dec.)	81
p-Tolylisocyanotris{tris(*p*-chlorophenylphosphite)}palladium(0)	$Pd(CNC_7H_7)[P(OC_6H_4Cl)_3]_3$	White needles	105	81
p-Anisylisocyanotris{tris(*p*-chlorophenylphosphine)}palladium(0)	$Pd(CNC_7H_7O)[P(C_6H_4Cl)_3]_3$	Colorless crystals	90–100	86
p-Anisyltris(triphenylphosphite)-palladium(0)	$Pd(CNC_7H_7O)[P(OC_6H_5)_3]_3$	Colorless crystals	105–10	86
p-Anisyltris{tris(*p*-chlorophenylphosphite)}palladium(0)	$Pd(CNC_7O_7H)[P(OC_6H_3Cl)_3]_3$	Colorless crystals	100–5	86
Diiodobis(*p*-anisylisocyano)palladium(II)	$PdI_2(CNC_6H_5)_2$	Orange needles		1
Dichlorobis(*p*-tolylisocyano)palladium(II)	$PdCl_2(CNC_7H_7)_2$	Pale yellow needles		1
Dibromobis(*p*-tolylisocyano)palladium(II)	$PdBr_2(CNC_7H_7O)_2$	Pale yellow needles		1
Diiodobis(*p*-tolylisocyano)palladium(II)	$PdI_2(CNC_7H_7)_2$	Orange needles		1
Diiodobis(*p*-anisylisocyano)palladium(II)	$PdI_2(CNC_7H_7O)_2$	Orange needles		1
Diiodobis(*p*-chlorophenylisocyano)palladium(II)	$PdI_2(CNC_6H_4Cl)_2$	Orange needles		1

pure carbonyl does not exist. They are also the only known case of coordinatively unsaturated isocyanide compounds.

The preparation of these derivatives of palladium(0) (79,81,84) was only possible under strictly controlled conditions. In fact, the divalent derivatives, $PdX_2(CNR)_2$, cannot be reduced to the zero valent state by strong reducing agents in acid, neutral, or slightly alkaline medium. In strongly alkaline solution, however, the reduction takes place spontaneously, but only if more than two moles of isocyanides per palladium atom are present. With slightly less than two moles of isocyanides, not even a trace of $Pd(CNR)_2$ is obtained, whereas a 5% excess over 2.5 moles results in a 50% yield.

As starting material for the preparation of the zero valent compounds, the diiodobis(arylisocyano)palladiums were chosen, because of the ease of their preparation. The reaction sequence is thought to be:

$$PdI_2(CNR)_2 + 2\,KOH \longrightarrow Pd(OH)_2(CNR)_2 + 2\,KI$$

$$Pd(OH)_2(CNR)_2 + 3\,RNC \longrightarrow Pd(CNR)_4 + RNCO + H_2O$$

$$Pd(CNR)_4 \longrightarrow Pd(CNR)_2 + 2\,CNR$$

The bis(arylisocyano)palladiums are black-brown crystalline substances, stable to air, diamagnetic and practically insoluble in most solvents. The very few solvents which dissolve them, such as nitrobenzene and pyridine, cause complete decomposition, so that it was impossible to undertake measurements of molecular weights. The formulation of these compounds as derivatives of palladium(0) is confirmed by their reaction with iodine. In alcoholic suspension they take up exactly one mole of iodine per palladium atom, yielding iodo compounds, $PdI_2(CNR)_2$, identical with those used as starting material in their preparation:

$$Pd(CNR)_2 + I_2 \longrightarrow PdI_2(CNR)_2$$

On reaction with derivatives of trivalent phosphorus, such as triarylphosphines and triarylphosphites, a partial or complete displacement of the isocyanide occurs, and new mixed and symmetrical derivatives of palladium(0) are formed (83,86). As shown by the following examples, the course of the reaction, as well as the products obtained, varies much with the substituting ligand:

$$(p\text{-}CH_3C_6H_4NC)_2Pd + 3\,(p\text{-}ClC_6H_4O)_3P \longrightarrow (p\text{-}CH_3C_6H_4NC)[(p\text{-}ClC_6H_4O)_3P]_3Pd$$

$$(p\text{-}CH_3C_6H_4NC)_2Pd + 4\,(C_6H_4O)_3P \longrightarrow [(C_6H_4O)_3P]_4Pd + 2\,p\text{-}CH_3C_6H_4NC$$

$$(p\text{-}CH_3C_6H_4NC)_2Pd + 3\,(p\text{-}ClC_6H_4)_3P \longrightarrow [(p\text{-}ClC_6H_4)_3P]_3Pd + 2\,p\text{-}CH_3C_6H_4NC$$

A somewhat analogous reaction probably takes place with a large excess of isocyanide: in fact, the $Pd(CNR)_2$ compounds dissolve in pure liquid aryl isocyanides to give yellow crystalline substances which could not be investigated because they are stable only in presence of the excess of isocyanide. It is likely, however, that these unstable compounds are the tri- and tetracoordinate $Pd(CNR)_3$ and $Pd(CNR)_4$.

Among the hypotheses that have so far been advanced on the structure of the bis(arylisocyano)palladium, two seem the most plausible: (*1*) the palladium atom is coordinatively unsaturated and forms only two linear bonds, and (*2*) the palladium atom reaches the E.A.N. of xenon through four metallic bonds to other palladium atoms and two coordinative bonds to isocyanide molecules. This polymeric structure would account for the insolubility of these complexes. The elucidation of the stereochemistry of these interesting compounds must, however, await an X-ray structure determination.

3. Platinum

a. Compounds of the Type $PtX_2\cdot 2CNR$

The alkaline salts of the tetrahalogeno-, tetranitro-, and tetracyanoplatinic(II) acids react readily with isocyanides, yielding very stable compounds of general formula $PtX_2.2CNR$ (X = Cl, Br, I, NO_2, CN). Those in which X is Cl, Br, I, and CN were obtained in two forms, one dimeric and ionic, $[Pt(CNR)_4][PtX_4]$, and the other monomeric and a nonelectrolyte, $PtX_2(CNR)_2$. The nitro derivatives were obtained only in the nonionic form. In several cases the monomeric $PtX_2(CNR)_2$ were isolated in two modifications of different colors and crystal forms, possibly the *cis-trans* isomers expected for compounds of such a type. The direct esterification of the acid $H_2[Pt(CN)_4]$ with ethanol has also been tried, but the compounds obtained do not appear to be isocyanide derivatives (20).

(*1*) *Compounds with X = Halogen Atom.* On treating a concentrated aqueous solution of sodium or potassium tetrachloroplatinate(II) or tetrabromoplatinate(II), or an alcoholic solution of sodium tetraiodoplatinate(II), with a slight excess of alkyl (12,13) or aryl

TABLE XI
Isocyanide Compounds of Platinum

Name	Formula	Color and crystal form	M.p. or dec. temp., °C.	
Dichlorobis(methylisocyano)platinum(II)	$PtCl_2(CNCH_3)_2$	Colorless crystals	233 (dec.)	13
Dicyanobis(methylisocyano)platinum(II)	$Pt(CN)_2(CNCH_3)_2$	Colorless needles		14
Dicyanobis(ethylisocyano)-platinum(II)	$Pt(CN)_2(CNC_2H_5)_2$	Colorless needles		14
Dicyanobis(*tert*-butylisocyano)platinum(II)	$Pt(CN)_2(CNC_4H_9)_2$	Yellow crystals		14
Dichlorobis(ethylisocyano)-platinum(II)	$PtCl_2(CNC_6H_5)_2$	Colorless crystals Yellow needles	257–8 219–20	101
Dibromobis(phenylisocyano)platinum(II)	$PtBr_2(CNC_6H_5)_2$	Colorless crystals	245	101
Diiodobis(phenylisocyano)-platinum(II)	$PtI_2(CNC_6H_5)_2$	Yellow large crystals Yellow fine needles	241	101
Bis(triiodo)bis(phenylisocyano)platinum(II)	$Pt(I_3)_2(CNC_6H_5)_2$	Purple-red needles		101
Dinitrobis(phenylisocyano)platinum(II)	$Pt(NO_2)_2(CNC_6H_5)_2$	Yellow needles Dark red needles	155 (dec.)	101
Tetrakis(methylisocyano)-platinum(II) tetrachloroplatinate(II)	$[Pt(CNCH_3)_4][PtCl_4]$	Red tablets		13

Tetrakis(methylisocyano)platinum(II) picrate	$[Pt(CNCH_3)_4][OC_6H_2(NO_2)_3]_2$	Yellow crystals	13
Tetrakis(*tert*-butylisocyano)platinum(II) picrate	$[Pt(CNC_4H_9)_4][OC_6H_2(NO_2)_3]_2$	Yellow crystals	13
Tetrakis(*tert*-butylisocyano)platinum(II) tetrachloroplatinate(II)	$[Pt(CNC_4H_9)_4][PtCl_4]$	Red crystals	13
Tetrakis(phenylisocyano)platinum(II) tetrachloroplatinate	$[Pt(CNC_6H_5)_4][PtCl_4]$	Blue-violet powder	101 57
Tetrakis(phenylisocyano)platinum(II) tetrabromoplatinate	$[Pt(CNC_6H_5)_4][PtBr_4]$	Brown-violet powder	101
Di-μ-hydrazidobis(bismethylisocyanoplatinum(II)) chloride with 2 moles HCl	$[(CH_3NC)_2Pt(NHNH_2)_2Pt(CNCH_3)_2]Cl_2 \cdot 2\ HCl$	Colorless prisms	15
Di-μ-hydrazidobis(bisethylisocyanoplatinum(II)) chloride with 2 moles HCl	$[(C_2H_5NC)_2Pt(NHNH_2)_2Pt(CNC_2H_5)_2]Cl_2 \cdot 2\ HCl$	White needles	15
Di-μ-hydrazidobis(tetrakismethylisocyanoplatinum(II)) chloride octahydrate	$[(CH_3NC)_4Pt(NHNH_2)_2Pt(CNCH_3)_4]Cl_2 \cdot 8\ H_2O$	Red prisms	15

(continued)

TABLE XI (*continued*)

Name	Formula	Color and crystal form	M.p. or dec. temp., °C.	Ref.
Di-μ-hydrazidobis(tetrakis-methylisocyano)platinum(II)) iodide tetrahydrate	$[(CH_3NC)_4Pt(NHNH_2)_2Pt(CNCH_3)_4]I_2 \cdot 4\ H_2O$	Brown-red needles		15
Di-μ-hydrazidobis(tetrakis-methylisocyano)platinum(II)) perchlorate dihydrate	$[(CH_3NC)_4Pt(NHNH_2)_2Pt(CNCH_3)_4](ClO_4)_2 \cdot 2\ H_2O$	Red needles		15
Di-μ-hydrazidobis(tetrakis-ethylisocyanoplatinum(II)) chloride	$[(C_2H_5NC)_4Pt(NHNH_2)_2Pt(CNC_2H_5)_4]Cl_2$	Yellow-orange needles		15
Di-μ-hydrazidobis(tetrakis-ethylisocyanoplatinum(II)) iodide	$[(C_2H_5NC)_4Pt(NHNH_2)_2Pt(CNC_2H_5)_4]I_2$	Yellow needles		115
Di-μ-hydrazidobis(tetrakis-ethylisocyanoplatinum(II)) nitrate dihydrate	$[(C_2H_5NC)_4Pt(NHNH_2)_2Pt(CNC_2H_5)_4](NO_3)_2 \cdot 2H_2O$	Red prisms		15
Di-μ-hydrazidobis(tetrakis-ethylisocyanoplatinum(II)) perchlorate	$[(C_2H_5NC)_4Pt(NHNH_2)_2Pt(CNC_2H_5)_4](ClO_4)_2$	Red prisms and needles		15
Di-μ-hydrazidobis(tetrakis-ethylisocyanoplatinum(II)) tetrachloroplatinate (II)	$[(C_2H_5NC)_4Pt(NHNH_2)_2Pt(CNC_2H_5)_4][PtCl_4]$	Red crystals		15

isocyanides (57,101), intensely colored substances, of composition corresponding to $PtX_2.2CNR$, separate at once. The aryl derivatives are apparently amorphous and practically insoluble in water; both are insoluble in all organic solvents. For these compounds, a saline structure of tetrahalogenoplatinates(II) of tetraisocyanoplatinum(II) was proposed on the basis of chemical behavior (13).

In fact, when treated in aqueous solution with tetraamminoplatinum chloride, $[Pt(NH_3)_4]Cl_2$, both the purple-red $PtCl_2(CNCH_3)_2$ and the blue-violet $PtCl_2(CNC_6H_5)_2$, give the green tetrachloroplatinate(II) of tetraamminoplatinum(II) $[Pt(NH_3)_4][PtCl_4]$ (Magnus' salt), thus proving the presence of the anion $[PtCl_4]^{2-}$. Although the chloride of tetraisocyanoplatinum could not be isolated from the solution, the reaction may be considered to be:

$$\underset{\text{red insoluble}}{[Pt(CNCH_3)_4][PtCl_4]} + [Pt(NH_3)_4]Cl_2 \longrightarrow \underset{\text{green insoluble}}{[Pt(NH_3)_4][PtCl_4]} + [Pt(CNCH_3)_4]Cl_2$$

The presence of the cation $[Pt(CNR)_4]^{2+}$ was proved by addition of sodium picrate to the purple-red $PtCl_2(CNCH_3)_2$ in aqueous solution; the picrate of tetrakis(methylisocyano)platinum(II) separated in yellow crystals sparingly soluble in water. The reaction may be written:

$$[Pt(CNCH_3)_4][PtCl_4] + 2\,NaOC_6H_2(NO_2)_3 \longrightarrow [Pt(CNCH_3)_4][\{OC_6H_2(NO_2)_3\}_2] + Na_2[PtCl_4]$$

On prolonged heating at 110–150° in the dry state, or on boiling for several hours in chloroform, the red-violet salts, $[Pt(CNR)_4][PtX_4]$, are converted into pale yellow crystalline substances of identical composition (13,101). These compounds are soluble in most organic solvents and insoluble in water. They are diamagnetic, nonelectrolytes, and monomeric in solution, and must be considered as the dihalogenodiisocyanoplatinum(II) compounds, $PtX_2(CNR)_2$. Many of them have been isolated in two crystal forms, often of slightly different colors, very easily converted into each other. It is not known whether they are just dimorphic forms, or the *cis-trans* isomers expected for the square planar dihalogendiisocyanoplatinums.

The yellow $PtCl_2(CNCH_3)_2$, when treated in aqueous solution with an excess of methyl isocyanide and then with sodium picrate, gives the picrate of tetrakis(methylisocyano)platinum(II), which shows that the following reactions have taken place (13):

$$\mathrm{PtCl_2(CNCH_3)_2 + 2\,CNCH_3 \longrightarrow [Pt(CNCH_3)_4]Cl_2}$$

$$\mathrm{[Pt(CNCH_3)_4]Cl_2 + 2\,NaOC_6H_2(NO_2)_3 \longrightarrow [Pt(CNCH_3)_4][\{OC_6H_2(NO_2)_3\}_2] + 2\,NaCl}$$

(2) Compounds with $X = NO_2$. Potassium tetranitroplatinate(II) reacts with isocyanides in aqueous solution (101), yielding nonionic monomeric compounds of formula $Pt(NO_2)_2(CNR)_2$. The dinitroisocyanoplatinum(II) compounds exist in two forms of different colors and solubilities, easily converted into each other.

(3) Compounds with $X = CN$. The reaction between potassium tetracyanoplatinate(II) (14) and methyl and ethyl isocyanide in water yields directly the monomeric dicyanodiisocyanoplatinum(II) compounds, $Pt(CN)_2(CNR)_2$. They are fluorescent, colorless, crystalline substances, soluble in methanol, slightly soluble in water and chloroform. These compounds are extremely stable and are decomposed only by a concentrated solution of potassium cyanide. Unlike the analogous halogeno derivatives, they do not react with an excess of isocyanide to give the tetraisocyanoplatinum(II) cation, $[Pt(CNR)_4]^{2+}$. The methyl derivative was also obtained by alkylation of silver tetracyanoplatinate(II) with methyl iodide:

$$\mathrm{Ag_2[Pt(CN)_4] + 2\,CH_3I \longrightarrow Pt(CN)_2(CNCH_3)_2 + 2\,AgI}$$

The reaction between potassium tetracyanoplatinate(II) in aqueous solution and *tert*-butyl isocyanide gives as first product the tetracyanoplatinate(II) of tetrakis(*tert*-butylisocyano)platinum(II), in bright red crystals insoluble in all solvents. The saline structure of this compound was determined by treating it with sodium picrate in water; as in the case of the analogous chloro compounds, the picrate of tetrakis(*tert*-butylisocyano)platinum separated in yellow crystals. On long standing in water, alcohol, or chloroform, the bright red salt, $[Pt(tert\text{-}C_4H_9NC)_4][Pt(CN)_4]$, was converted slowly into the the nonionic monomeric form, $Pt(CN)_2(tert\text{-}C_4H_9NC)_2$. The dicyanobis(*tert*-butylisocyano)platinum(II) is a colorless crystalline product, more soluble than its methyl and ethyl analogues. A mixture of the saline and nonsaline forms is obtained by treating platinum(II) cyanide, $Pt(CN)_2$, with *tert*-butyl isocyanide.

The nonsaline monomeric form is also formed, quite unexpectedly, in another way. The bright red crystalline tetrachloroplatinate of tetrakis(*tert*-butylisocyano)platinum, which may be easily prepared from $K_2[PtCl_4]$ and *tert*-C_4H_9NC in water, behaves in fact in a way different from the other compounds of this type. It does not change into the nonionic yellow form on boiling in solvents, and on treating with an excess of isocyanide dissolves, giving the following reactions:

$$[Pt(\textit{tert}\text{-}C_4H_9NC)_4][PtCl_4] + 4(\textit{tert}\text{-}C_4H_9NC) \longrightarrow 2[Pt(\textit{tert}\text{-}C_4H_9NC)_4]Cl_2$$

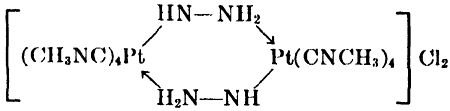
$$[Pt(\textit{tert}\text{-}C_4H_9NC)_4]Cl_2 + 2H_2O \longrightarrow Pt(CN)_2(\textit{tert}\text{-}C_4H_9NC)_2 + 2C_4H_9OH + 2HCl$$

This is perhaps the only case of an isocyanide hydrolyzing neatly into hydrocyanic acid and alcohol.

b. Compounds Containing Alkyl Isocyanides and Hydrazine

A remarkable series of complex salts of platinum(II), containing alkyl isocyanides and hydrazine, was described by Chugaev and coworkers (15).

On treating a concentrated aqueous solution of sodium or potassium tetrachloroplatinate(II) first with methyl isocyanide and then with hydrazine, a bright red crystalline product was obtained, which was formulated as the chloride of di-μ-hydrazidobis(tetrakismethylisocyano)platinum(II):



This compound, on reaction with sodium iodide and sodium perchlorate, gave the corresponding iodide and perchlorate. The iodide was obtained as a tetrahydrate, $[Pt_2(N_2H_3)_2(CNCH_3)_8]I_2 \cdot 4H_2O$, brown-red in presence of water, emerald-green when dry; the perchlorate was obtained as a red-colored dihydrate, $[Pt_2(N_2H_3)_2(CNCH_3)_8](ClO_4)_2 \cdot 2H_2O$, with green reflectances.

Analogous compounds were obtained with ethyl isocyanides. The chloride of di-μ-hydrazido-bis(tetrakisethylisocyano)platinum(II) was not isolated, but the corresponding iodide, perchlorate, nitrate, and tetrachloroplatinate(II) were obtained in a pure state. These compounds are all very stable and beautifully crystalline, soluble in water, slightly soluble in alcohol. Their stability, as well as the conditions under which they are formed, is rather surprising. In fact, hydrazine in presence of isocyanides would have been expected to reduce platinum(II) to the zero valent isocyanide compounds, or at any rate—in case these should not be stable—to metal.

Another peculiar feature of these compounds is the unusual coordination number six, exhibited by platinum(II). In this respect it is interesting that on treatment with concentrated hydrochloric acid, the salt $[Pt_2(N_2H_3)_2(CNCH_3)_8]Cl_2$ loses isocyanide giving the similar chloride of di-μ-hydrazido-bis(bismethylisocyano)platinum(II), $[Pt_2(N_2H_3)_2(CNCH_3)_4]Cl_2$, in which platinum(II) shows its usual coordination number, four.

The salts of the cation $[Pt_2(N_2H_3)_2(CNCH_3)_4]^{2+}$ are stable yellow crystalline substances, less soluble in water than the corresponding salts of the cation $[Pt_2(N_2H_3)_2(CNCH_3)_8]^{2+}$. By action of alkali in presence of methyl isocyanide, they are reconverted into the salts of di-μ-hydrazidobis(tetrakismethylisocyano)platinum(II), so that the reaction may be considered to be a sort of equilibrium:

$$\underset{\text{red}}{[Pt_2(N_2H_3)_2(CNCH_3)_8]Cl_2} \xrightleftharpoons[\text{NaOH} + CH_3NC]{\text{HCl}} \underset{\text{yellow}}{[Pt_2(N_2H_3)_2(CNCH_3)_4]Cl_2} + 4\ CH_3NC$$

On the whole, the structures attributed to these interesting compounds—though quite possible—do not seem thoroughly proved and deserve further investigation.

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The Effect of Inner Orbital Splitting on the Thermodynamic Properties of Transition Metal Compounds and Coordination Complexes

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I. Introduction

Over one-half of the elements in the periodic table belong to one of the five transition groups. These elements have an incompletely filled inner *d* or *f* electron shell which is responsible for most of their characteristic properties. The purpose of this article is to show how chemical thermodynamic properties are modified by the incomplete inner shell.

The theoretical basis for the treatment is called ligand field theory (1,2). The main feature of the theory is that the ligands in a complex ion, or the anion neighbors of a transition metal cation in a crystal, are considered to produce a field which causes the inner orbitals to split into several groups with different energies. The field may be considered to arise either from the electrostatic charge distribution of the ligands or from the chemical bonding between central ion and ligands. The origin of the field has been discussed in many places before, and need concern us no further (2). The splitting results in a stabilization of the inner electrons compared to the energy they would have had in the absence of the crystal field (3,4). In the important case of the inner *d* shell, this contribution to the stability of the substance may amount to as much as 100 kcal./mole.

Under isothermal conditions, the electric field of the surroundings must always reduce the energy of the electrons of an atom if they are in an orbitally degenerate state. Electronic orbital degeneracy occurs in the partially filled *p*, *d*, and *f* shells except when these are half filled. The *p* shell cannot be treated by ligand field theory because the bonding of *p* electrons is much more important than the splitting, and the *p* orbitals of the metal ion are strongly mixed with orbitals of the other atom in the bond. The *d*, and particularly the *f*, orbitals in chemical compounds bear a sufficiently close resemblance to the orbitals of the free ions so that ligand field theory is applicable to them.

We can imagine that formation of a chemical compound at first changes the energy of all the inner *d* or *f* orbitals by the same amount, without splitting. This energy change is a large quantity, since it may correspond, for example, to a part of the coulomb energy of a crystal lattice. The splitting of the orbitals may be imagined to follow later, whereupon the electrons fall into the lowest available components of the original level, thereby losing some energy. We will show later how the heat due to the splitting may be separated from other heat terms.

The removal of orbital degeneracy occurs in any of the common geometries, from the axial fields produced by a single atom in the vicinity of the transition metal ion to the highly symmetrical field produced by the F^- ions in the fluorite crystal.

In the important case of six-fold octahedral coordination, the five orbitals of the d shell which correspond to the same energy in the free ion are split by the ligands into a lower group of three and an upper group of two. The reason for this mode of splitting may be seen from the shapes of the d orbitals themselves. When expressed in a way appropriate for the introduction of a cubic field perturbation, they have the following forms:

$$\begin{aligned} t:&\quad f(r)(xy/r^2),\ f(r)(xz/r^2),\ f(r)(yz/r^2) \\ e:&\quad f(r)[(x^2 - y^2)/r^2],\ f(r)[(2z^2 - x^2 - y^2)/r^2] \end{aligned} \tag{1}$$

The group called t are physically equivalent, as they simply correspond to different orientations of the same function. In the field of an octahedron of ligands, they must have the same energy because the charge distribution in such a field is the same along any Cartesian axis. The functions of the e group may be derived from the spatially equivalent set $(x^2 - y^2)$, $(y^2 - z^2)$, $(z^2 - x^2)$ by taking a combination of the last two such that it is orthogonal to the first. Thus the two e functions also are degenerate simply because of their spatial orientation.

Electrons in the t orbital have the lower energy because the probability maxima occur away from the ligands (in $x = y$ direction, etc.) and the ligands tend to repel electrons. The e functions, however, have their maxima along the directions to the ligands, and are thus raised in energy by the mutual repulsion between electron and ligand. The ratio of the energy of lowering the t orbitals to the energy of raising the e orbitals equals the inverse ratio of their degeneracies and is therefore 2:3.

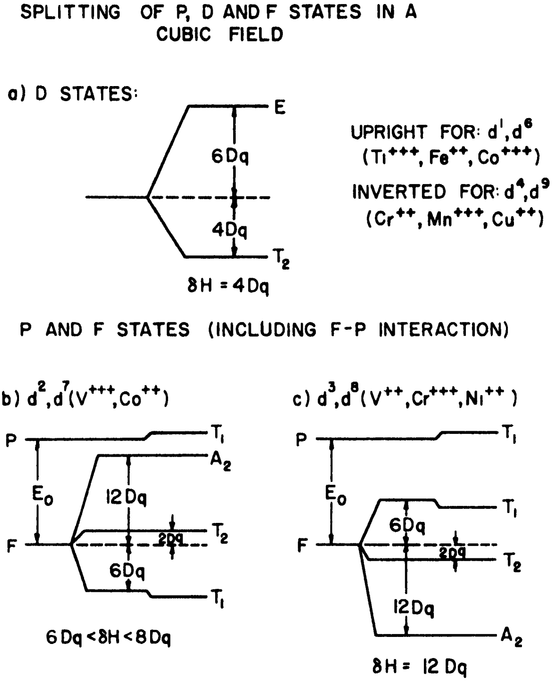

Fig. 1. Splitting of *P*, *D*, and *F* states in a cubic field. These diagrams are appropriate for octahedral coördination as they stand, and when inverted are appropriate for tetrahedral or cubic coördination. The value of δH is the energy of the lowest component below the unperturbed level. The strongest bands of the spectrum are due to transitions from the lowest to the higher levels shown here. Other levels (not shown) give rise to weak bands. The method of deriving Dq from the spectrum is to identify the bands and to divide the observed energy by the corresponding theoretical factor. Part a of the figure serves as a splitting diagram for both a *D* state and a *d* orbital. The *t* orbitals are lowest in an octahedral field, and highest in a tetrahedral field.

The result of the splitting is shown in Figure 1a. The diagram applies not only to the *d* orbitals but to all *D* states of an ion. The *t* orbitals (or T_2 state) are lowered by $4Dq$, and the *e* orbitals (or *E* state) are raised by $6Dq$, giving the ratio 2:3 previously mentioned. The parameter Dq measures the strength of the ligand, or crystal, field.

If Figure 1a is considered as an orbital energy diagram, the origin of the thermodynamic stabilization effect can be seen for any *d* electron configuration. The energy of the first electron will be lowered in the crystal field by $4Dq$. Two would have their energy lowered by a total of $8Dq$, and three by $12Dq$, etc. The maximum number in the t orbitals is six. Addition of more than six results in a reduction of the total stabilization by $6Dq$ for each electron beyond the first six.

The heat increment tending to stabilize the ion, $-\delta H$, thus becomes

$$-\delta H = -(4n_t - 6n_e)Dq \tag{2}$$

where n_t and n_e are the numbers of electrons in t and e orbitals, respectively.

This simple picture of a way to reduce the energy of the d electrons has omitted consideration of an important factor, namely, the interelectronic repulsion. The largest energies of this type occur when two electrons occupy the same orbital. The first three electrons may be placed in each of the three different t orbitals. However, the fourth must either be raised in energy by $6Dq$ to place it in an e orbital, or paired with another electron in a t orbital at the expense of the pairing energy. The ground state of the four-electron system corresponds to the distribution having the lesser of the two energy increments.

In order to understand how electronic interactions modify the simple orbital picture, consider the free ion, whose electronic states are determined almost entirely by electronic interactions (spin-orbit coupling may be ignored in a first approximation). The lowest state is that in which the electrons interfere with each other the least. This requirement is expressed by Hund's rule: "The lowest state of the free ion is one having the maximum number of unpaired electron spins, and of these it is the one having the greatest orbital angular momentum." In the presence of a weak crystal field it is found that Hund's rule still holds, and the energy, $6Dq$, lost by promoting an electron into an e orbital is less than the amount which would be lost if the electrons were paired in the t orbitals. This is the most common case among the elements of the $3d$ transition group and accounts for the paramagnetism of their salts. In the $4d$ and $5d$ transition groups, however, the pairing energies are smaller because of the greater spatial extent of the d orbitals, and the Dq values are larger, with the result that the paired state is often favored over the unpaired.

The results of the theory for the case of unpaired spins in octahedral crystal fields are illustrated by Figure 1a,b,c and are shown in Table VI (page 401). The figure shows the way in which the ground states of the free ions split in the field. Since the electron repulsion determines the ground state, the diagram automatically includes electron repulsion effects. Only *S*, *D*, and *F* states may occur as ground states of ions having d^n configurations. As an *S* state is not split in the crystal field, it is not shown in the figure. Those ions having *F* ground states also have an excited *P* state of the same multiplicity. In the presence of the crystal field, the *P* state mixes with a certain component of the *F* state, and thereby contributes a small amount to the stabilization of the ground state whenever that component is the lowest one. This effect is shown in Figure 1b. The thermodynamic stabilization varies between $6Dq$ and $8Dq$ depending upon the importance of this mixing. In general the thermodynamic stabilization value, $-\delta H$, for the case of unpaired spins is given by

$$-\delta H = -xDq \tag{3}$$

where the factor x is given in Table VI, and Dq may be determined from spectra. Values of Dq are given in Tables V and VII (pages 398 and 402).

If the crystal field remains strictly octahedral, spin pairing by strong fields (5) can only occur in the configurations d^4, d^5, d^6, and d^7. Its occurrence could be illustrated by a diagram similar to Figure 1, except that an *excited* state of the free ion having paired spins would split to such an extent that its lowest component becomes the ground state. It is more instructive, however, to return to Figure 1a, considering it as an orbital energy diagram, and then to add on the energies of electron pairing in the t orbitals. For example, the configuration d^4 in a weak octahedral field becomes t^3e (all electrons unpaired), but in a strong field the lowest configuration is t^4 or, more explicitly, $t_1t_2t_3^2$. The change from t^3e to t^4 has resulted in a reduction of crystal field energy by $10Dq$, but at the cost of putting two electrons in the orbital t_3. The d^4 ion will, therefore, have its spins paired if

$$10Dq > P \tag{4}$$

where P is the energy of electron repulsion added in passing from t^3e to t^4. The pairing energies are given in Table VIII (page 403) in terms of atomic spectral parameters. It is not strictly correct to use the values of the parameters for the free ion, since in a strong crystal field covalency will result in lowered values, but the important qualitative results are not affected by this approximation. The thermodynamic stabilization value for the case in which the spins are paired is

$$-\delta H = -(4n_t - 6n_e)\,Dq + P \tag{5}$$

where P is the total pairing energy. This is the modification of eq. 2 which is made necessary by the occurrence of the electron repulsion energy. Whether the spins become paired or not is determined by the relative values of δH given by eqs. 3 and 5.

In order to isolate the part of the heat of a reaction which is due to crystal effects we must have a suitable standard for comparison from which crystal field effects are absent. Since the field cannot be turned off and on at will, the standards must be reactions different from the ones studied but preferably as similar as possible to them. For example, the heats of lattice formation of the transition metal monoxides may be compared with those of CaO and ZnO, and since Mn^{2+} (d^5) has no crystal field stabilization (S state), MnO is also a suitable standard. An interpolation curve free of crystal field effects may be estimated for the entire series of oxides by plotting the data for these three against atomic number. The deviations of the lattice energies of the other oxides from the interpolation curve are considered to be the crystal field effects sought for. An independent check on this procedure is provided by the use of spectroscopic data.

We have gathered together the best available data on the thermodynamic properties of transition metal compounds and complex ions and have determined their crystal or ligand field effects by methods similar to that outlined in the preceding paragraph. The results are in reasonably good agreement with theory and with the spectroscopic data. We feel that the ligand field effect is sufficiently well established by these results that its magnitude may be predicted with confidence in new cases and used to help in the estimation of unknown thermodynamic properties. There are also some deviations from the simple theory we have applied here, and their explanation may lead to new knowledge. There are many ions for which no thermodynamic or spectroscopic data are available, and of course the theory cannot be tested for these. It would be particularly interesting if both kinds of data were available for the 4*d* and 5*d* transition groups. Finally, the details of the correlation of thermodynamic and spectroscopic properties could be pursued further if more accurate and more extensive data were available for the 3*d* transition group.

II. The Effect of Crystal Fields on the Thermodynamic Properties of Solids

In order to find the effect of the crystal fields on the binding energies of solids, one must begin with the atoms in a reference state from which the crystal field is absent, namely, an infinitely dilute gas. The heat of formation from this state will contain the full contribution of the crystal field. The particular gaseous reference state chosen is somewhat arbitrary. One could choose, for example, the neutral atoms; the resulting heat of formation of the compound is called its bonding energy. On the other hand, the ions in their classical valence states could be used, the heat of formation in this case being called the lattice energy.

A. THE GAS PHASE REFERENCE STATE

An important restriction on the choice of reference state is that the same number of electrons must be present in the *d* shell of the free ion as are present in the *d* shell of the combined ion. This requirement sometimes necessitates the use of an excited state of an atom for its reference state. For example, to calculate the bonding energy of divalent transition metal halides, the electronic configurations of the neutral atom reference states should be $3d^n4s^2$, where n is the number of *d* electrons in both free atom and compound. One state of this configuration is the ground state for most of the neutral atoms, except in the case of Cr and Cu where the lowest of these states lie 23.2 and 33.4 kcal./mole, respectively, above the ground state. In order to use the neutral atom reference state, the bonding energies must be increased by these values for Cr and Cu. We will refer to the resulting heats of formation as the "corrected bonding energies."

Neutral atoms cannot be used as the reference states for trivalent compounds because the required configurations are not known. The energies of the $3d^n4s^2$ configurations are known for most of the M^+ ions and can be used to define a corrected bonding energy for these compounds, although a correction must be made for each member of the transition series in this case.

The difficulties with the corrections to the bonding energy are avoided if one uses the doubly or triply ionized states of the free atoms as the reference states for divalent or trivalent compounds. The familiar lattice energies are then obtained. Another advantage of this choice is that the lattice energies may be analyzed in terms of the classical theory of ionic solids, as is done in Section II-G.

Values of *Dq*, the crystal field splitting parameter, are obtainable from the thermodynamic data, as will be shown in Section II-C. We wish to point out here that the values obtained are nearly the same whether the corrected bonding energy or the lattice energy is used. The slight differences which exist are due to the fact that the energy differences between the two reference states do not vary exactly linearly with atomic number, and this in turn may possibly be traced to changes in the importance of configuration interaction through the transition series.

B. SURVEY OF THE LATTICE ENERGIES

We will first present the empirical data on lattice energies and point out the features which merit consideration. The lattice energy is the heat of the reaction

$$\mathrm{M}^{n+}{}_{g} + n\,\mathrm{X}^{-}{}_{g} \longrightarrow \mathrm{MX}_{n,s} \tag{6}$$

for the case of singly charged anions. These heats are given in Tables I–IV.* (They are enthalpies and include the small $P\Delta V$ terms.) Only the first (3*d*) transition series is represented: the other two series (4*d* and 5*d*) will be mentioned in Section II-E. The lattice energies are obtained from the standard heat of formation of MX_n and the heats of formation of M^{n+} and X^- from the elements in their standard states. The heat of formation of MX_n will be called ΔH_f, and the heats of preparation of M^{n+} and X^-, $H_P{}^{n+}$ and $H_P{}^-$, respectively. The quantity of $H_P{}^{n+}$ includes a small correction for

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* In Tables I–IV the left-hand column gives the value of $H_P{}^+$ for the cation; the bottom row gives the $H_P{}^-$ value for the anion. At the intersection of row and column is given minus the heat of formation of the compound from the elements, and below it, in italics, is the lattice energy. The lattice energy is the sum of the other three quantities. The error in the heat of formation is given to the right of each value. It is the largest error in the lattice energy, and in every case is the total uncertainty in lattice energy. The type of crystal structure where known is indicated by an abbreviation next to the lattice energy value for the compound concerned.

TABLE I[a]
Lattice Energies of Divalent Halides[b]

	H_P^{2+}	F		Cl		Br		I	
Ca	459.7	290.2 ± *622.9*	4. F	190.6 ± *533.7*	2. CaCl	161.3 ± *510.4*	3. CaCl	127.8 ± *490.7*	3. CdI
Ti	587.9	198. *658.9*	15.	120.6 *591.9*	2. CdI	95. *572.3*	10.	61. *552.1*	10. CdI
V	603.8	180. *661.8*	20.	117. *609.2*	20.	97. *595.2*	20. CdI	61. *573.0*	20. CdI
Cr	635.1	182. *690.1*	3.	95. *613.5*	4.	74. *598.5*	5.	53.3 *591.6*	1.4
Mn	601.6	190. *664.6*	6. Ru	113. *598.0*	2. CdCl	91. *582.0*	2.	59. *563.8*	3. CdI
Fe	658.9	168. *699.9*	5. Ru	81.5 *623.8*	0.4 CdCl	59.0 *607.3*	0.5 CdI	30. *592.1*	2. CdI
Co	681.2	158. *712.2*	5. Ru	78. *642.6*	4. CdCl	55.5 *626.1*	4. CdI	24. *608.4*	4. CdI
Ni	701.4	158.0 *732.4*	1.5 Ru	73.0 *657.8*	0.5 CdCl	54.2 *645.0*	2. CdI	21. *625.6*	2. CdCl
Cu	732.3	128. *733.3*	4.	50. *665.7*	3. CuCl	33.7 *654.9*	2.5 CuCl	2. *637.5*	2.5
Zn	664.7	176. *713.7*	5. Ru	99.5 *647.6*	0.3 CdCl	78.2 *632.3*	0.5	50.0 *616.9*	0.3
$2H_P^-$		−127.		−116.6		−110.6		−96.8	

[a] Lattice energies in italics. See footnote on page 389.

[b] Crystal structure: F = fluorite, CaCl = calcium chloride, CdCl = cadmium chloride, CdI = cadmium iodide, Ru = rutile, CuCl = copper chloride.

TABLE II[a]

Lattice Energies of Divalent Chalconides[b]

	H_P^{2+}	O		S		Se		Te	
Ca	459.7	151.9 ±	0.7	115.3 ±	3.	74.7 ±	6.	(65) ±	8.
		842.6	R	*728.0*	R	*699.4*	R	*652.7*	R
Ti	587.9	123.9	0.8	(52)					
		942.8	R	*792.9*					
V	608.8	106.	5.						
		945.8	R		N				
Cr	635.1	<90.			N		N		N
		<956.							
Mn	601.6	92.	1.	49.5	.5	28.	3.	(22.5)	
		924.6	*R*	*804.1*	R,W,Z	*794.6*	R,W,Z	*752.1*	N
Fe	658.9	63.5	.5	22.8	.3	18.	1.	18.6	
		953.4	R	*834.7*	N	*841.9*	N	*805.5*	N
Co	681.2	57.2	.5	21.	2.	10.	2.5	9.	2.5
		969.4	R	*855.2*	N	*856.2*	N	*818.2*	N
Ni	701.4	57.5	.5	22.2	1.4	10.	3.	9.	3.
		989.9	R	*876.6*	N	*876.4*	N	*838.4*	N
Cu	732.3	37.1	.8	11.6	1.	5.5	2.		
		1000.4		*896.9*		*902.8*			
Zn	664.7	83.2		48.5	3.	34.	4.	30.	
		978.9	W,Z	*866.2*	W,Z	*863.7*	Z	*822.7*	W,Z
H_P^-		231.		153.		165.		128.	

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[a] Lattice energies in italics. See footnote on page 389.

[b] Crystal structure: R = rock salt, N = nickel arsenide, W = wurtzite, Z = zinc blende.

TABLE III[a]
Lattice Energies of Nitrates, Carbonates, Sulfates[b]

	H_P^{2+}	NO_3^-	CO_3^{2-}		SO_4^{2-}	
Ca	459.7	224.0	288.5	0.7	342.	3.5
		683.7	*748.2*	C	*801.7*	
Ti	587.9					
V	608.8					
Cr	635.1					
Mn	601.6	166.3	213.9	1.2	254.2	1.
		767.9	*815.5*		*855.8*	
Fe	658.9		179.	3.	221.	6.
			837.9	C	*879.9*	
Co	681.2	102.9	173.	4.	208.	6.
		784.1	*854.2*		*889.2*	
Ni	701.4	102.2	163.	3.	213	5.
		803.6	*864.4*		*914.4*	
Cu	732.3	73.4	142.	10.	184.	2.5
		805.7	*874.3*		*916.3*	
Zn	664.7	115.1	194.2	1.	233.9	1.
		779.8	*858.9*	C	*898.6*	

[a] Lattice energies in italics. See footnote on page 389.
[b] C = calcite structure.

reaching the proper valence state, by taking into account the width of the lowest multiplet of $M^{n+}{}_g$. The details of the calculations and the sources of data are given in Section II-I. The lattice energy, U, is then found from the equation:

$$-U = H_P{}^{n+} + H_P{}^{-} - \Delta H_f \tag{7}$$

The lattice energies of the divalent halides of the first transition group are plotted against atomic number in Figure 2. The atomic number is a reasonable abscissa to use, since we expect to find some gradual changes in the properties of the compounds as electrons are added to the 3*d* shell. The variation observed in Figure 2 may be described as a steady increase in lattice energy with two humps superimposed on it.

If a straight line is drawn between the points for Ca^{2+} and Zn^{2+}, it passes just below the point for Mn^{2+}. These three ions have zero, five, and ten *d* electrons, respectively, and therefore have nondegenerate ground states. No crystal field stabiliza-

TABLE IV[a]
Lattice Energies of Trivalent Halides[b]

	H_P^{3+}	F		Cl		Br		I	
Sc	1105.1	367.	± 7.	221.	± 1.	179.4	± 1.	125.5	± 1.
		1281.6	ReO	*1151.2*		*1118.6*		*1085.4*	
Ti	1237.6	315.	15.	170.7	0.6	132.	10.	80.	20.
		1362.		*1233.4*	BiI	*1203.7*	BiI	*1172.4*	
V	1295.1	285.	30.	139.	20.	109.	20.		
		1389.6		*1259.2*		*1238.2*			
Cr	1350.6	266.	5.	135.	5.	91.	7.	47.5	1.7
		1426.1		*1310.7*	CrCl	*1275.7*	BiI	*1252.9*	
Mn	1381.1	238.	7.	110.	5.				
		1428.6		*1316.2*					
Fe	1365.5	235.	13.	95.7	1.	63.5	2.		
		1410.0	ReO	*1286.3*	BiI	*1263.1*			
Co	1453.8	187.	10.						
		1450.3	ReO						
Ni									
Cu									
Zn									
Ga	1388.1	255.	10.	125.	1.5	92.4	1.	51.	2.
		1452.6		*1338.2*		*1314.6*		*1293.9*	
$3H_P^-$		−190.5		−174.9		−165.9		−145.2	

[a] Lattice energies in italics. See footnote on page 389.

[b] Crystal structure: CrCl = chromium trichloride, BiI = bismuth triiodide. ReO = rhenium trioxide

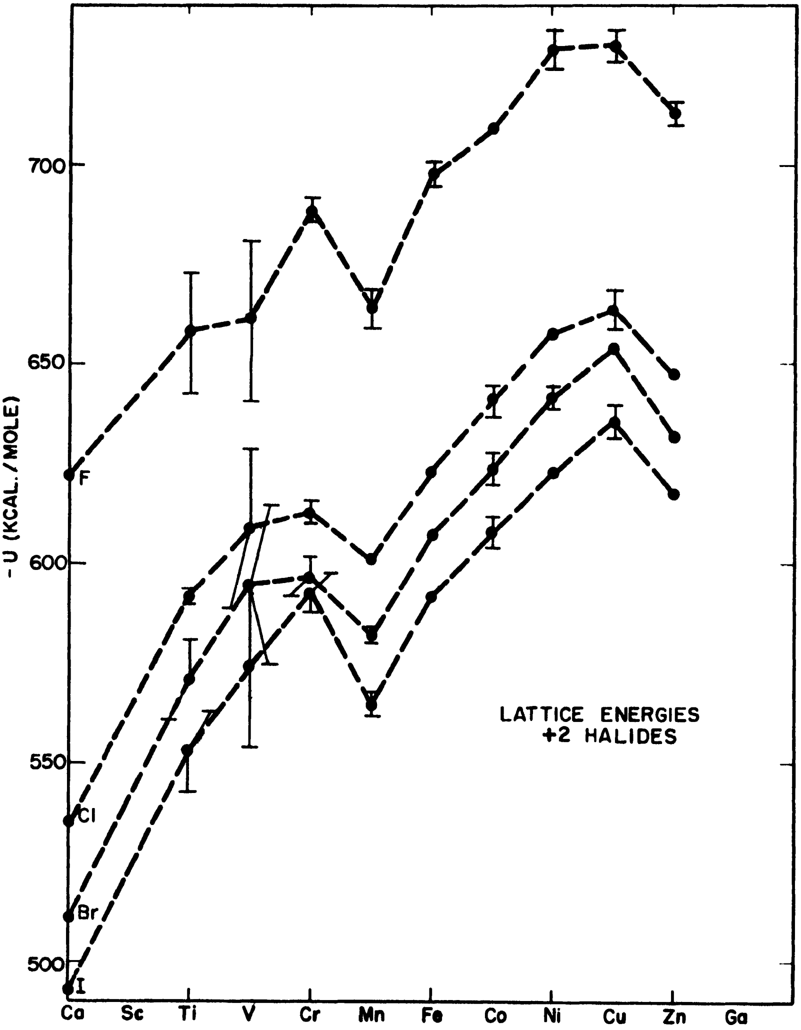

Fig. 2. Lattice energies of the divalent halides.

tion could be expected for them. (The magnetism of Mn^{2+} shows that its spins are unpaired so that Table VI (page 401) applies.) For all the other ions, the heats of formation of their halides fall above the Ca–Mn–Zn lines, indicating greater stability.

Similar though less complete data are presented for the divalent chalconides (Fig. 3) and the divalent sulfates, carbonates, and nitrates (Fig. 4). The point for Mn again falls very close to the line joining Ca and Zn except for the nitrates. The data for the latter may be in error, or some effect of unknown origin may come into play.

The increase in U from Mn^{2+} to Zn^{2+} compounds, which we will call E_r (Mn–Zn), is of the order of 50 kcal./mole, as shown in Table V. The height of the hump over the Mn–Zn line is also roughly the same throughout the entire group of M^{2+} compounds. The first half of the transition group is like the second half, although there are not so many data and their accuracy is not so great. The values of E_r (Ca–Mn) and E_r (Mn–Zn) are presented in Table V.

The trivalent halides (see Fig. 5) and the oxides M_2O_3 behave similarly to the divalent compounds. The trivalent ions having nongenerate ground states are Sc^{3+}, Fe^{3+}, and Ga^{3+}. There is a qualitative difference from the divalent case in that the Sc–Fe–Ga curve is much further from being a straight line, and the E_r value for the first half of the group is much greater than for the second half. The humps on the curves are about 50% larger than for the divalent compounds. The data are given in Table V.

In both the divalent and trivalent compounds the E_r values become progressively larger in the order $F < Cl < Br < I < O < S < Se < Te$.

By examining the lattice energy data for ions having nondegenerate ground states (d^0, d^5, d^{10}), we hope to derive an interpolation curve for Figures 2–5 which would give the lattice energy if there were no crystal field effects. The difference between the actual lattice energy and the appropriate point on the interpolation curve will be called δH and is interpreted as the contribution of the crystal field to the lattice energy. We assume that the interpolation curve is a monotonic function of the number of d electrons. Temporarily, we will assume that the straight line segments d^0–d^5 and d^5–d^{10} may be used.

A theory of this interpolation curve could be based upon the classical theory of ionic solids, but it would require considerable work on the theory of the repulsion constants and the van der Waals term for the transition metal ions. This has not been carried out to our knowledge. However, by using the empirical lattice energies (Tables I–IV), the E_r values can be analyzed into the part due to the change

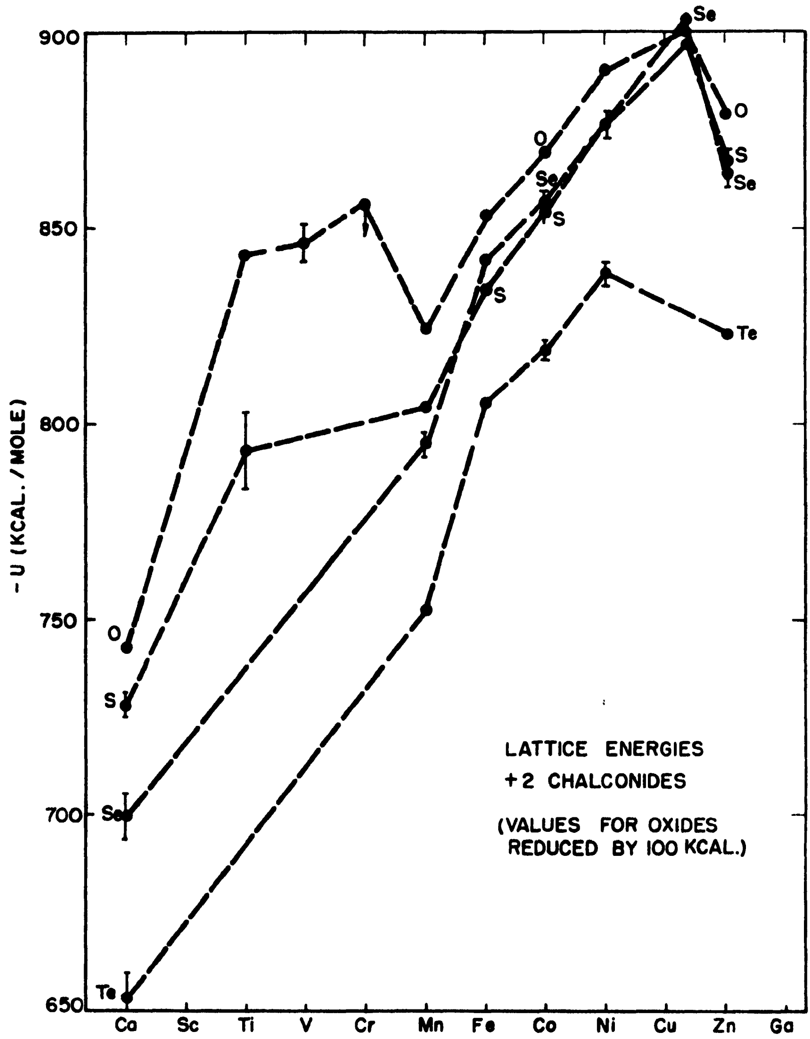

Fig. 3. Lattice energies of the divalent chalconides.

in radius (Madelung energy) and the part due to other effects, which we shall group under the term repulsion energy. It is found that for the divalent oxides E_r is due to the change in Madelung energy, but that for the divalent sulfides and selenides the Madelung and repulsion energies each contribute substantially the same amount.

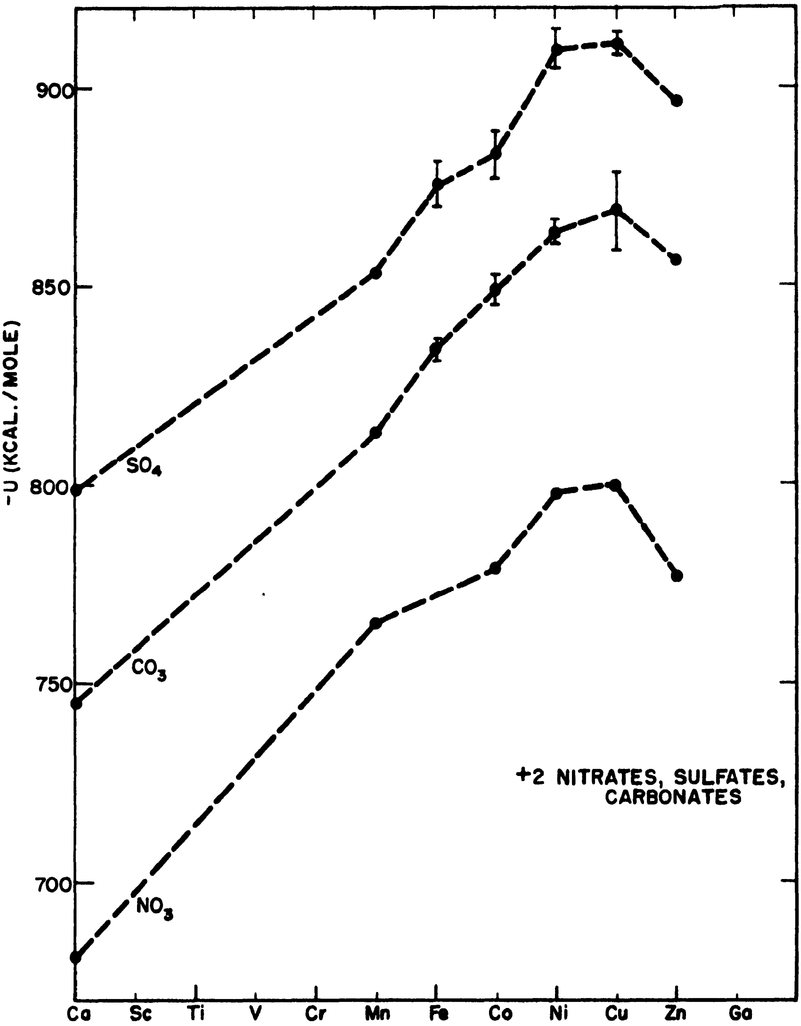

Fig. 4. Lattice energies of the divalent sulfates, nitrates, and carbonates.

The available thermodynamic data are not entirely independent of each other. Heats of formation of halides, for example, are usually determined from a heat of solution of the halide in water and a hydration energy, determined from the heat of solution of the metal in acid. The heats of formation of all the halides of a metal are there-

TABLE V
Analysis of Lattice and Hydration Energy Data

Compound	E_r, kcal./mole		Thermodynamic *Dq*, kcal./mole *Divalent Ions*						
	(Ca–Mn)	(Mn–Zn)	Ti	V	Cr	Fe	Co	Ni	Cu
Fluoride	41.7	49.1	2.8		5.7	6.3	4.0	3.2	4.9
Chloride	64.3	49.6	4.6		4.7	4.0	3.5	2.5	4.7
Bromide	71.6	50.3	4.5		5.1	3.8	3.4	2.7	5.4
Iodide	73.1	54.1	4.9		7.1	4.6	3.3	2.5	5.1
Sulfate	54.1	42.8				3.9	2.3	2.7	4.4
Carbonate	67.3	43.4				3.4	3.1	1.9	4.0
Nitrate	84.2	11.9					1.6	2.4	4.7
Oxide	82.0	54.3				4.5	3.3	2.7	5.5
Sulfide	76.1	62.1				4.6	3.8	2.9	7.2
Selenide	95.2	69.1				8.4[a]	4.8	3.4	8.8
Telluride	99.4	70.6				9.8[a]	5.4	3.6	
Hydrate	64.5	47.1	5.4	3.2	4.5	4.2	3.5	2.8	4.2
Spectroscopic *Dq* (hydrate)			*(3.5)*	*3.4*	*4.0*	*2.84*	*2.84*	*2.44*	*3.70*

Compound	E_r, kcal./mole (Sc–Fe)	E_r, kcal./mole (Fe–Ga)	Thermodynamic *Dq*, kcal./mole *Trivalent Ions* Ti	V	Cr	Mn	Co
Fluoride	128.4	42.6	14	8	5.6	7.4	8.0
Chloride	135.1	51.9	14	8	6.5	9.5	
Bromide	144.5	51.5	14	9	5.9		
Iodide	150[b]	58[b]	14		6.5		
Oxide ($^1/_2$ mole)	160[c]	53	21	10	7	10	
Hydrate	123	62	14	8	7.1	8.8	11[a]
Spectroscopic *Dq* (hydrate)			*5.8*	*5.1*	*5.0*	*6.0*	*5.5*

[a] Spins are probably paired, but these values are computed as for the rest of the table assuming they are unpaired.

[b] As FeI_3 is not stable, the E_r values were estimated.

[c] The U value of Sc_2O_3 is not known, and the E_r (Sc–Fe) value was estimated.

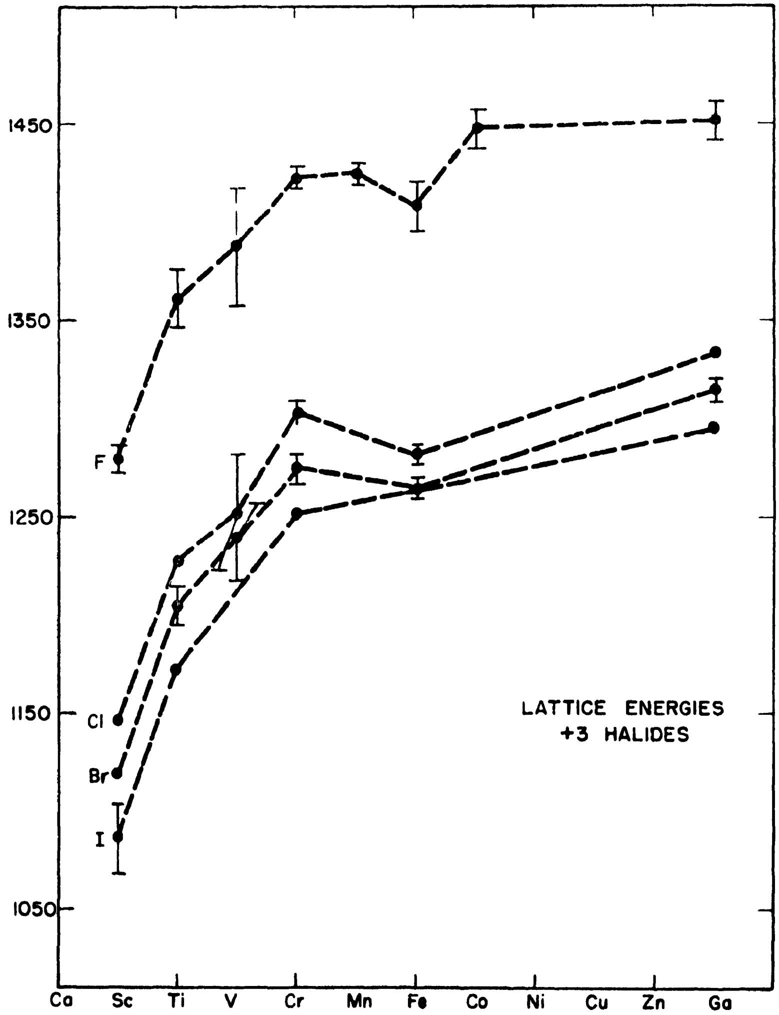

Fig. 5. Lattice energies of the trivalent halides.

fore usually dependent upon one value of the hydration energy of the cation, thus containing all of the errors associated with it. This fact may explain the seemingly low values of the lattice energies of all scandium compounds, as they all depend upon a single reported value of the heat of solution of scandium in acid. The data presented here should be examined with this fact in mind. The actual details may be found from the references given in Section II-I.

C. CRYSTAL FIELD EFFECTS

The *d* electrons of an ion are stabilized in the crystal field by the amount δH, which depends on the number of *d* electrons and the parameter Dq. The δH values given by crystal field theory are found in Table VI in units of Dq. These values are appropriate for the maximum number of unpaired *d* electrons, i.e., the weak field case. The compounds of the first transition series usually display the maximum spin multiplicity. Those of the second and third series, however, usually display maximum spin pairing. Table VIII gives δH values for the latter case.

TABLE VI
Values of δH in Dq Units for High Spin Complexes and Compounds

Number of *d* electrons	δH (octahedral site)	δH (cubic o tetrahedral site)
0	0	0
1	4	6
2	6–8	12
3	12	6–8
4	6	4
5	0	0
6	4	6
7	6–8	12
8	12	6–8
9	6	4
10	0	0

Table VI shows the theoretical stabilization energies for ions in both octahedral and tetrahedral sites. In the special cases of two and seven electrons in octahedral sites (or for three and eight electrons in tetrahedral sites), the stabilization energy may vary from $6Dq$ to $8Dq$ depending upon the magnitude of Dq. For small Dq the correct value is close to 6, and for large Dq it is close to 8. An exact formula may be written, but for the sake of simplicity, we will use the value 7 in all cases.

In addition to the stabilization of the *d* electrons, there is another but smaller effect of the partly filled *d* shell. This is the reduction of the ionic radius by the crystal field. The magnitude of this term will be discussed in Section II-G, but for the present it may be ignored.

Values of the parameter *Dq* derived from the observed δH values through the use of Table VI are given in Table V. The accuracy of these values is not high, since the entire uncertainty in *U* is included in δH. The *Dq* values derived from the spectra of hydrated ions are also given in Table V and the few values of *Dq* derived from spectra of solids are collected in Table VII for comparison with the thermodynamic values. In spite of the presence of errors there are trends common to the *Dq* values from both sources and their absolute values do not differ greatly. This is encouraging, since the two sets of numbers are derived from entirely independent data. The following points are worthy of notice:

TABLE VII
Comparison of Spectroscopic and Thermodynamic *Dq* Values
(in kcal./mole)

Compound	Spectroscopic *Dq*	Thermodynamic *Dq*
NiF_2	2.29	3.2
$NiCl_2$	2.21	2.5
$NiBr_2$	2.23	2.7
NiO	2.56	2.7
CoF_2	2.44	4.0
$CrCl_3$	4.1	6.5
Cr_2O_3	4 88	7 0

1. The thermodynamic values decrease steadily from the beginning to end of the transition series except for the d^4 and d^9 ions (Cr^{2+}, Cu^{2+}, and Mn^{3+}), which have higher than average values (see Section II-D). This agrees with the trend of the spectroscopic values.
2. The thermodynamic values are all somewhat higher than the spectroscopic values. This is probably an indication that the interpolation curve is not exactly a straight line; furthermore, the ionic radius effect (Section II-G) contributes to the thermodynamic, but not to the spectroscopic, value.
3. The thermodynamic values for the divalent fluorides are unaccountably high.
4. Two *Dq* values which appear much too high are those for Fe-

Se and FeTe. Although these compounds are difficult to characterize and do not exist as exactly stoichiometric substances, we will assume that experimental errors do not account for the large discrepancies. Another possibility is that the Fe^{2+} ions are not in their state of maximum spin, but that the spins are partially or wholly paired. Magnetic measurements, in fact, show that the full spin of four electrons per ion is not present (7), although one cannot draw more definite conclusions from the data. In a case in which all the spins are paired, δH is given, not by $4Dq$, but by $24Dq - P$, where P is the pairing energy (Table VIII). For Fe^{2+}, $P = 110$ kcal./mole if one uses the parameter values appropriate for the free ion. However, such values are 20–30% too high for the ion in a crystal, so that P is reduced to about 80 kcal./mole. If the value of Dq is assumed to be the same as for the sulfide, $24Dq = 108$ kcal./mole and $24Dq - P = 28$ kcal./mole. Since $4Dq = 18$ kcal./mole, the stabilization of the paired state is greater than that of the unpaired, and the former will be the ground state. Actually, the case of a partially quenched spin seems to be possible for these compounds because of their peculiar crystal structure.

TABLE VIII

Values of δH in Terms of B, C, and Dq for Low Spin Complexes and Compounds

Number of *d* electrons				
Oct.	Tetr.	Pairing energy	Crystal field energy	Total δH
0	10	0	0	0
1	9	0	$4Dq$	$4Dq$
2	8	0	$8Dq$	$8Dq$
3	7	0	$12Dq$	$12Dq$
4	6	$6B + 5C$	$16Dq$	$16Dq - 6B - 5C$
5	5	$15B + 10C$	$20Dq$	$20Dq - 15B - 10C$
6	4	$5B + 8C$	$24Dq$	$24Dq - 5B - 8C$
7	3	$7B + 4C$	$18Dq$	$18Dq - 7B - 4C$
8	2	0	$12Dq$	$12Dq$
9	1	0	$6Dq$	$6Dq$

Typical values of the electrostatic interaction parameters (B and C) for d electrons (kcal./mole)

Ion	V^{2+}	Mn^{2+}	Ni^{2+}	V^{3+}	Mn^{3+}	Ni^{3+}	Zr^0	Y^+
B	2.19	2.49	2.98	2.49	2.80	3.24	0.84	0.78
C	9.42	11.14	14.06	11.08	12.92	15.80	5.88	6.00

5. The thermodynamic *Dq* values for Ti^{3+} and V^{3+} are much too high. Possibly the interpolation curve for trivalent ions should not be a straight line, but should be similar to the curve of "corrected" heats of hydration shown for these ions in Figure 7 (page 418). This curve was obtained by subtracting the spectroscopic *Dq* values from the heats of hydration. Alternatively, there could be a large error in the lattice energy values for Sc^{3+} compounds. If the values were raised by about 40 kcal./mole, reasonable *Dq* values and a straight line interpolation curve would be obtained.

D. THE EFFECT OF DIFFERENT CRYSTAL STRUCTURES ON THE COMPARISON OF LATTICE ENERGIES

There is no series of compounds of the transition metals having the same crystal structure from d^0 to d^{10}. The crystal structure of each compound is indicated where known in Tables I–IV (8). For example, the divalent oxides occur with the NaCl structure except for ZnO, which has the wurtzite structure. One wonders what errors are introduced by comparing lattice energies corresponding to different crystal structures. The greatest possibility of error is in those series in which the coordination number changes from one member to another.

For practically all of the halides, the coordination number is six throughout, and the lattice energy should not differ greatly among the several structures. Since the crystal field contributions depend, for all practical purposes, upon only the nearest neighbors, the relation between *Dq* and δH should be nearly the same for all the halides.

The NiAs structure occurs for those sulfides, selenides, and tellurides which have degenerate ground states, but not for Ca, Mn, or Zn. The metal atoms in this structure are six-coordinated to anions, but two other metal atoms are a distance slightly larger than the anion–cation distance. The reason for the occurrence of this structure is not fully understood, but it may be suggested that the close approach of metal atoms provides another mechanism by which the *d* shell energy may be lowered. If this is true, there could be some change in the relation between δH and *Dq* from that of Table VI, but we believe it to be small.

Calculations of the change in lattice energy of a crystal resulting from a change in structure have been made several times (9). The total change in lattice energy for AgF going from the NaCl (six-coordinated) to the zinc blende structure (four-coordinated) is +8.3 kcal./mole, and for many other crystals it is smaller. An energy difference of this order would have an appreciable but not overwhelming effect on the thermodynamic *Dq* values. For the oxides, the interpolation curve in Figure 3 would not rise so high in the region of Zn, and the *Dq* values near this end would be raised; the rest of the curve would not be affected. Calculations of the differences between lattice energies are not very reliable, and the results have only order of magnitude significance.

The only structures which have eight- or four-fold coordination occur among ions having nondegenerate ground states, for example, CaF_2 (fluorite structure), ZnO (wurtzite), and MnS (which occurs with NaCl, wurtzite, or zinc blende structures). This last case is particularly interesting, as all three structures of MnS have lattice energies within a few kcal./mole of each other. The fluorite structure becomes less stable through the transition series because of the decreasing ionic radius. The two four-coordinated structures, wurtzite and zinc blende, become more stable owing both to the radius effect and to a tendency to form sp^3 bonds.

The occurrence of the six-coordinated structures, rutile, CdI_2, NiAs, and NaCl, is probably aided by the "octahedral site preference energy" of the transition metal ions. The origin of this site preference is, again, the splitting of the *d* shell, as explained in Section II-H. This site preference is greatest for Ni^{2+} and Cu^{2+}, where the opposing tendency to form a four-coordinated structure is probably greatest, and it may therefore be an important factor in maintaining six-coordinated structure types throughout the transition series.

The ions having d^4 or d^9 configurations have a doubly degenerate ground state (E_g) in octahedral coordination. This type of state is especially sensitive to the distortions introduced by the Jahn-Teller effect, with the result that the ions are better described as ellipsoids than as spheres. As a result the crystal structures of compounds of Mn^{3+}, Cr^{2+}, and Cu^{2+} are found to be distortions of more common structures. The coordination octahedra have tetragonal or rhombic distortions. Both the thermodynamic and the spectroscopic *Dq* values are apparently considerably higher for compounds of these ions than for their neighbors, as shown in Table V. The *Dq* values decrease rather uniformly from the light to the heavy members of the first transition series, except that they appear about 50% too high at

d^4 and d^9. The additional amount over what would be expected is caused by the distortions of lower symmetry.

E. LATTICE ENERGIES FOR THE SECOND AND THIRD TRANSITION SERIES

Thermodynamic data for compounds of the second and third transition series are scarce; consequently, very little can be said about the crystal field effects. The lattice energies for the series II and III dichlorides and for the series II monoxides are plotted against atomic number in Figure 6. The E_r values are worth comparing for the three series. For MCl_2 they are:

I E_r (Ca–Zn) = 132.2

II E_r (Sr–Cd) = 94.3

III E_r (Ba–Hg) = 138.6

The large value for series III is undoubtedly a result of the lanthanide contraction. The interpolation curve for series III should therefore include a jog between La and Hf to take this into account. A guess as to the amount needed is given in Figure 6.

Compounds of the $4d$ and $5d$ transition groups do not always possess the maximum value of the spin multiplicity. In fact, the usual rule is maximum spin pairing. The thermodynamic stabilization of d electrons in octahedral and tetrahedral fields with maximum spin pairing is given in Table VIII. The pairing energies, P, have been calculated in terms of the Racah parameters, which, in turn, may be estimated from atomic spectra (6). Some respresentative values of the Racah parameters are given in Table VIII. These parameters essentially measure the interelectronic repulsion between two d electrons; and the higher their value, the more difficult it is to place two electrons in the same orbital. The pairing energies are less for series II and III than for I, and the Dq values greater; hence, both factors favor a spin-paired state. When spin pairing occurs, the minimum at the d^5 ion will be less well marked than otherwise.

The crystal structures of the series II and III compounds are not well known. Furthermore, in the few cases for which structures have been determined, they are not often analogous to those of the first transition series. For example, PdO and PtO have approximately square planar coordination of the metal by oxygen instead of the Na-

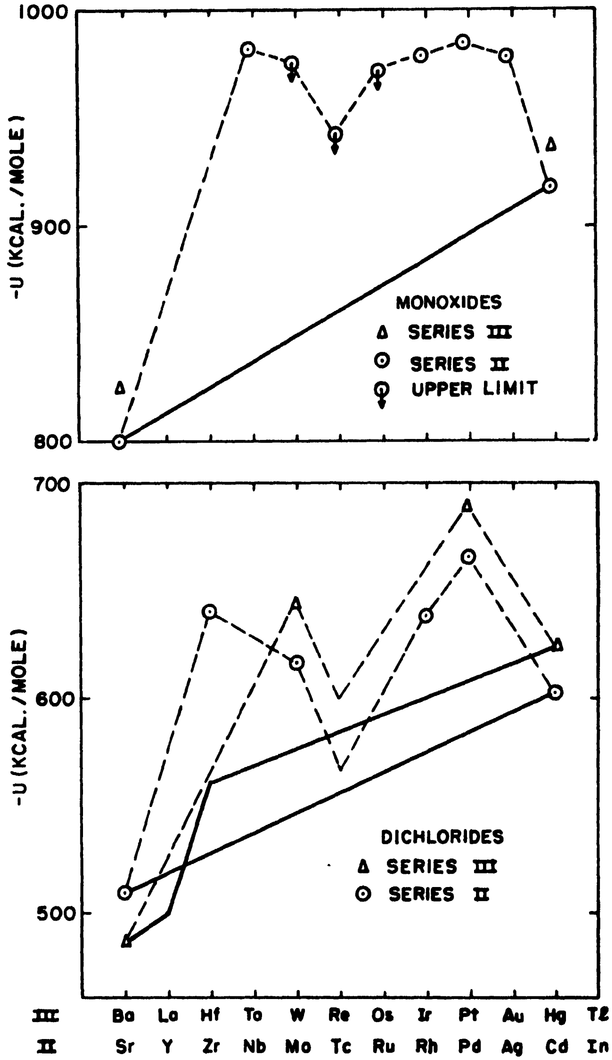

Fig. 6. Lattice energies of the monoxides and dichlorides of the second (II) and third (III) transition series.

Cl structure possessed by NiO in the same column of the periodic table. There is good reason to believe that the square (or rectangular) coordination is itself a result of the interaction between the *d* shell and the surrounding O atoms. It is a Jahn-Teller distortion of a state of the d^8 configuration in which the spins are paired.

In spite of these complications and the scarcity of data there are good indications that the ligand field stabilization is stronger in series II and III than in I. Values of Dq determined spectroscopically are about 50% larger for II and III than for I among compounds having the same structure and number of d electrons (10). This fact is in agreement with the indications of the thermodynamic data.

It would be most interesting to have both thermodynamic and spectroscopic data for some of the ions near the center of these two series in order to observe whether or not there is a real cusp at d^5, as suggested by Figure 6, and to compare the results with the predictions of the pairing theory (Table VIII).

F. THE RARE EARTH COMPOUNDS

It has long been recognized that there are gradual changes in the chemical properties of the series of trivalent rare earth ions passing from La^{3+} to Lu^{3+}. The main cause of this trend has been considered to be the reduction in ionic radius, the "lanthanide contraction." Unfortunately, there are not enough data to calculate the energy of lattice formation from a common valence state of the free metal ions. Therefore it is not possible to demonstrate crystal field effects in the rare earth compounds. The probable order of magnitude of δH is known from electron spin resonance and optical spectra. In $Nd(BrO_3)_3 \cdot 9H_2O$ we expect a crystal field stabilization of 1.5 kcal., for example. Unlike all the other cases, the entropy effects at room temperature due to having many low-lying electronic levels are almost as large as δH in these compounds.

G. ANALYSIS OF THE CRYSTAL FIELD STABILIZATION

Throughout Sections II-A–II-F we have, in effect, compared the lattice energies of actual transition metal compounds with a hypothetical substance having no crystal field stabilization. Here we intend to examine such a comparison more carefully. The main complication to be considered is that the crystal field not only reduces the energy of the d electrons, but also reduces the ionic radius (6,11). The latter effect must be accompanied by an increase in the Madelung energy stabilizing the crystal and an increase in the repulsion term tending to destabilize it. So far, we have only considered the energy reduction of the d electrons by the crystal field.

Let us assume that there is a hypothetical standard crystal having properties very similar to those of the real crystal, but not having a stabilizing effect due to the electrostatic field. The lattice energies of a series of such crystals may be imagined to fall on a smooth curve drawn from d^0 to d^5 to d^{10}. If we take the crystals to be cubic, the energy depends only on one parameter, such as the cation–anion distance, R, and the energy of the hypothetical crystal may be written as:

$$U_1(R_0) = F(R_0) \tag{8}$$

where R_0 is the equilibrium distance. The real crystal has an additional energy term from the crystal field. We will assume that the same function, F, describes the variation of the other energy terms with R. The energy of the real crystal is then:

$$U_2(R_e) = F(R_e) - E_c(R_e) \tag{9}$$

where R_e is the equilibrium internuclear distance in the real crystal. The energy difference in which we are interested is:

$$\Delta U = U_2(R_e) - U_1(R_0) = -E_c(R_e) + F(R_e) - F(R_0) \tag{10}$$

Up to the present we have assumed that the crystal field stabilization was completely accounted for by the electronic term $-E_c(R_e)$. Now we have the additional term $F(R_e) - F(R_0)$. Elementary considerations show that this term is positive, since $F(R_0)$ is the minimum value of F by hypothesis. A detailed calculation using the Madelung and Born repulsion energy terms shows the additional term to be about 12% of E_c in the case of NiO. The classical theory of ionic crystals therefore predicts that the total stabilization by the crystal field will be somewhat less than the electronic stabilization.

The data presented earlier, based upon a straight line for the interpolation curve, contradict this prediction, since the thermodynamic Dq values were found consistently to be higher than the spectroscopic. If the added term $F(R_e) - F(R_0)$ were certain to be positive, we would be justified in using a convex-upward interpolation curve such that the thermodynamic Dq is reduced to a value below the spectroscopic value. We do not believe, however, that the oversimplified theory used here provides any such certainty. A more detailed analysis of the chemical bonding in the crystal would be necessary. A conclusion we can draw, however, is that the term $E_c(R_e)$ is considerably larger than the other terms. This result justifies our assumption that the spectroscopic value of δH should nearly equal the thermodynamic value. We will leave it to some future investigation to determine a more exact relationship between them. In the practical use of crystal field theory, we recommend a linear interpolation curve, spectroscopic δH values, and an empirically determined correction if high accuracy is desired.

H. INFLUENCE OF *d* ORBITAL SPLITTING ON CRYSTAL STRUCTURE

The extra stability conferred by splitting the *d* shell apparently affects the structures of some crystals. The clearest example occurs in oxides with the spinel structure having the general formula AB_2O_4, where A is typically a divalent ion, and B trivalent. The structure may be considered to be a cubic close-packed lattice of oxygen atoms whose octahedral and tetrahedral interstices are in part filled by metal atoms. In a "normal" spinel, the divalent A ions occupy sites with tetrahedral coordination, while the B ions occupy sites with octahedral coordination. This arrangement may be symbolized as $A[B_2]O_4$, where the bracket indicates octahedral coordination. It is found that the so-called inverse structure, $B[AB]O_4$, also occurs wherein the A ions have moved to octahedral sites, and in turn half the B ions move to tetrahedral sites. The equilibrium

$$\underset{\text{Normal}}{A[B_2]O_4} \rightleftharpoons \underset{\text{Inverse}}{B[AB]O_4} \qquad (11)$$

is controlled mainly by the change in internal energy, the entropy change being comparatively small. In the case of transition metal ions, the internal energy contains a crystal field contribution, δH, whose magnitude depends upon the coordination number. The difference

$$\delta H \text{ (octahedral)} - \delta H \text{ (tetrahedral)}$$

has been termed the site preference energy of an ion. The relative site preference energy of ions A and B enters into the determination of the position of the equilibrium in reaction 11 among spinels. It has been shown that a remarkably complete account of the distribution of transition metal cations in spinels is given by consideration of this one factor alone (12,13).

There are undoubtedly other systems where crystal field effects determine which of several probable structures are realized. We have already mentioned the persistence of six-coordinated structures in the first transition series as evidence for this.

Another type of influence is the distortion of the crystal by the nonspherically symmetric *d* shell of certain transition metal ions. Relatively large distortions occur because d^4 and d^9 ions, which would normally be octahedrally coordinated, or d^1 or d^6 ions, normally in tetrahedral coordination, are unable to maintain regular symmetry in their immediate environment. Smaller effects of the same nature result if d^1, d^2, d^6, and d^7 ions are in octahedral coordination, or d^3, d^4, d^8, and d^9 ions are in tetrahedral coordination. These distortions are regarded as manifestations of the Jahn-Teller effect. A review of the data is to be found in ref. 14.

I. SOURCES OF DATA

1. *Calculation of Lattice Energies from Thermodynamic Data*

In this section we shall describe the calculation of the lattice energies and heats of hydration and give the sources of thermodynamic data used in the calculations. Since all of our conclusions are based upon an interpretation of rather small trends in the lattice energies, we have attempted to collect the best data available and to estimate the reliability of each datum.

TABLE IXA
Heats of Formation of Divalent Ions
at 298°K. in Valence States
$H_{P^{2+}} = S^{298} + I_1 + I_2 + P^+ + 3.0 - N$ (kcal./mole)

Element	S^{298}	$I_1 + I_2$	N	P^+	$H_{P^{2+}}$
Ca	42.2	414.5	0.	0.	459.7
Ti	112.6	471.7	0.3	0.9	587.9
V	122.75	482.7	0.7	0.9	608.8
Cr	95.0	536.1	0.	1.0	635.1
Mn	66.73	531.9	0.	0.	601.6
Fe	99.83	555.1	0.2	1.2	658.9
Co	101.6	574.3	<0.1	2.3	681.2
Ni	101.26	594.4	<0.1	2.8	701.4
Cu	81.1	645.8	0.	2.4	732.3
Zn	31.18	630.5	0.	0.	664.7

Using the Born-Haber cycle, we may consider the lattice energies as being composed of three parts: (*a*) $H_P{}^+$, heat of preparation of the positive ion, (*b*) $H_P{}^-$, heat of preparation of the negative ion, and (*c*) ΔH_f, heat of formation of the compound—all from the elements in their standard states at 298°K. (15). The lattice energy is then given by eq. 7. In Table IX we give values of $H_P{}^+$ and $H_P{}^-$ for the ions of interest. The values of ΔH_f are given in the tables referring to particular compounds (Tables I–IV).

TABLE IXB
Heats of Formation of Trivalent Ions
($H_P{}^{3+}$) in Valence States (at 298°K.)
$H_P{}^{3+} = S^{298} + I_1 + I_2 + I_3 + P^+ + 4.3 - N$ (kcal./mole)

Element	S^{298}	$I_1 + I_2 + I_3$	N	P^+	$H_P{}^{(3+)}$
Sc	82.0	1019.0	0.2	0.	1105.1
Ti	112.6	1120.4	0.3	.6	1237.6
V	122.75	1167.5	0.7	1.2	1295.1
Cr	95.0	1249.6	0.	1.7	1350.6
Mn	66.73	1308.6	0.	1.5	1381.1
Fe	99.83	1261.5	0.2	0.	1365.5
Co	101.6	1346.4	<0.1	1.5	1453.8
Ni	101.26	1428.0	<0.1	2.3	1528.6
Cu	81.1	1494.9	0.0	3.7	1584.0
Zn	31.18	1545.8	0.0	3.2	1584.5
Ga	65.0	1318.9	0.1	0.	1388.1

TABLE IXC
Heats of Formation of Negative Ions ($H_P{}^-$) in Vapor at 298°K.
$H_P{}^- = H_A - E^0 - {}^5/_2 n\, RT$ (kcal /mole)

Element	H_A	E^{298}	$H_P{}^-$
F	18.3	81.8	−63.5
Cl	29.01	87.3	−58.3
Br	26.71	82.0	−55.3
I	25.48	73.9	−48.4
O	59.16	−172.	231.
S	53.25	−100.	153.
Se	48.37	−117.	165.
Te	47.6	−80.	128.

The formula for $H_P{}^+$ for divalent ions is

$$H_P{}^{2+} = S + I_1 + I_2 + 2(^5/_2RT) + P^{2+} - N \qquad (12)$$

where S is the heat of sublimation of the metal at 298°K.; I_1 and I_2 are the first and second ionization potentials; the term $2(^5/_2\,RT)$ corrects the ionization potentials to 298°K.; P^{2+} is the valence state preparation energy, i.e., the center of gravity of the ground state multiplet of the ion:

$$P^+ = \sum_J (2\,J + 1)E(J)/\sum_J (2\,J + 1) \qquad (13)$$

(this correction is necessary since we are ignoring effects of spin orbit coupling on the energies); and N is the electronic heat content of metal atoms at 298°K.

$H_P{}^{3+}$ is similarly defined as:

$$H_P{}^{3+} = S + I_1 + I_2 + I_3 + 3(^5/_2RT) + P^{3+} - N \qquad (14)$$

The ionization potentials were obtained from Moore's tables (16), and the valence state energies were computed from the energy levels given there. The heats of sublimation were obtained from the new compilation by Stull and Sinke (17).

The value of $H_P{}^-$ is given by

$$H_P{}^- = H_A - E^0 - {}^5/_2nRT \qquad (15)$$

where H_A is the heat of formation of the gaseous atoms at 298°K., and n is the number of charges on the ions. The electron affinities of the halogens are Brewer's (18) values, while those for O, S, and Se are Kapustinskii's (19). The value for Te was obtained by an extrapolation from the lattice energies of alkali earth chalconides and an approximate lattice energy for MgTe. Subsequent to the preparation of the table, new and better values of the double electron affinities of the chalcogens have appeared, as follows:

O^{2-} − 153 ± 7 (20)

S^{2-} − 99 ± 15 (21)

Se^{2-} − 117 ± 15 (21)

Te^{2-} − 97 ± 20 (21)

Our results are not affected by these changes, but individual lattice energies must be corrected. The heats of formation of gaseous atoms are taken from *NBS Circular 500* (22). The values of H_P^- for the halogens are practically the same as in the NBS tables except for the value for F^-. The value of 79.5 given there implies an electron affinity which is not consistent with the value calculated from the heats of formation given there for the alkali halides. The electron affinity calculated from these data is practically the same as Brewer's value, however. The E values for the chalcogens cannot be considered as reliable numbers. They are obtained from calculated lattice energies and from the Born-Haber cycle. The lattice energy calculations assume a purely ionic lattice, and this is undoubtedly a poor approximation in several cases. For the comparisons we have made, however, this uncertainty is of no consequence. For this reason also, we did not make any estimates of H_P^- for NO_3^-, CO_3^{2-}, and SO_4^{2-}, so that the so-called lattice energies given in Table III are not true lattice energies.

The heats of formation of chemical compounds, ΔH_f, are taken from *NBS Circular 500* (22) in most cases. The recent book, *Metallurgical Thermochemistry* by Kubachewski and Evans (23), supplied some new data and estimates of the reliability of the values. Other estimates of reliability were obtained from Brewer (18). The standard states used for computing heats of formation are the normal states of the elements at 298°K. and 1 atm. pressure.

The heat of hydration ΔH_H is the enthalpy change in the reaction:

$$M^{n+}_{g,v} + ne^-_g + nH^+_{aq} \rightarrow {}^n/_2H_{2g} + M^{n+}_{aq} \qquad (16)$$

where $M^{n+}_{g,v}$ means an n-fold ionized metal atom in the gaseous state and in its valence state (as defined by eq. 13).

This quantity is calculated from the reactions:

$$\begin{aligned} M_s &\xrightarrow{\qquad} M^{n+}_{g,v} + ne^-_g \qquad H_P^{n+} \\ M_s + n\,H^+_{aq} &\xrightarrow{\qquad} M^{n+}_{aq} + {}^n/_2\,H_{2,g} \qquad \Delta H_F \end{aligned} \qquad (17)$$

where ΔH_F is the heat of formation in solution and is equal to the heat of solution of the metal in acid, infinitely dilute. The heat of formation of H^+ in aqueous solution is set equal to zero. The heat of hydration is then given by

$$\Delta H_H = \Delta H_F - H_P^{n+} \qquad (18)$$

The values of ΔH_F are mainly from *NBS Circular 500* (22), but some estimates by Brewer (18) are included.

The only uncertainties of importance for use are in the heats of formation of the compounds. The estimated uncertainties are given next to ΔH_f in Tables I–IV and are represented as vertical lines in Figures 2–5.

2. The Dq Values

The method of obtaining *Dq* values from spectral data is given by Orgel (24) and is also shown in Figure 1, along with the formula for δH. The values for hydrated ions given in Table V are taken from Orgel's and from several other papers (10,25). It has been assumed that all the +2 and +3 ions are six-coordinated in aqueous solution. This assumption is supported by the identity of the spectra in solution with those of crystalline hydrates (25). It was found necessary to determine *Dq* values for several ions for which spectral data are not available. They were found by extrapolation of a plot of *Dq* vs. atomic number, such as the one given by Holmes and McClure (25), and by using the approximate relationship:

$$Dq_{3+}/Dq_{2+} = 1.5$$

The *Dq* value for octahedral coordination is the one most commonly quoted. However, tetrahedral and cubic coordination also occur. Very few experimental values for these coordination types exist. An approximate relationship between *Dq* values for regular four, six and eight coordination is the following, derived from the point charge model of the crystal field:

$$Dq\text{ (octahedral)} = -{}^9/_4 Dq\text{ (tetrahedral)} = -{}^9/_8 Dq\text{ (cubic)}$$

The sign change is quite important, as it has the effect of inverting the crystal field splitting.

In the case of octahedral d^4 and d^9 ions and of tetrahedral or cubic d^1 and d^6 ions a doubly degenerate E_g state is expected to lie lowest. Since this is subject to a large Jahn-Teller splitting, the coordination is not normally regular. The *Dq* value obtained from spectra, assuming regular coordination, will be overestimated, since a part of the splitting is due to other factors. However, very little error is made in estimating the δH value.

III. Hydration Energies

The hydration energy of an ion is defined for practical purposes as the heat of the reaction 16. It is the heat liberated when the gaseous ion in its valence state (eq. 13) is dissolved in water (26). Since the hydration sheath is very similar to the coordination shell in a crystal, the heats of hydration vary with atomic number in much the same way as do the lattice energies. The values of the heats of hydration for the divalent and trivalent ions of the first transition group are given in Table X, and they are plotted against atomic number in Figure 7. We have used the convention that the heat of formation of H^+ in aqueous solution is zero, following the usage of *NBS Circular 500* (22). It is shown in Table V that the values of E_r (Ca–Mn), E_r (Mn–Zn), and Dq (thermodynamic) for hydrated ions are quite similar to the values for the crystalline chlorides, both for divalent and trivalent ions.

TABLE X

Heats of Hydration (ΔH_H) at 298°K.

$-\Delta H_H = -\Delta H_F + H_P^+$ (kcal./mole)

	Divalent ions				Trivalent ions			
	H_P^{2+a}	$-\Delta H_F^{b}$		$-\Delta H_H^{2+}$	H_P^{3+a}	$-\Delta H_F^{b}$		$-\Delta H_H^{3+}$
Ca	459.7	129.8 ±	0.2	589.5				
Sc					1105.1	148.8 ±	1	1254
Ti	587.9	65	25	653	1237.6	96	5	1334
V	608.8	55	25	664	1295.1	65	25	1360
Cr	635.1	33	6	668	1350.6	61	5	1412
Mn	601.6	52	3	654	1381.1	24	3	1405
Fe	658.9	21	1	680	1365.5	11	2	1377
Co	681.2	16	3	697	1453.8	−21	4	1433
Ni	701.4	15	2	716				
Cu	732.3	−15.4	0.3	716.9				
Zn	664.7	36.4	0.2	701.1				
Ga					1389.1	50	3	1439

[a] Values from Table IX.

[b] Heat of formation in solution.

Values of Dq may be derived from absorption spectra of aqueous solutions of the ions and used to compute a δH value, which is independent of thermodynamic data. When this value is subtracted from the ΔH_H values, there result the heats of hydration which would be expected in the absence of a ligand field effect (25). These "corrected" ΔH_H values are plotted in Figure 7. They are seen to lie nearly on the straight lines Ca–Mn and Mn–Zn for the divalent ions, and somewhat above the Sc–Fe line for the trivalent ions. We have already mentioned these facts in Sections II-C and II-G in connection with the lattice energies, where they were taken to justify the use of straight line interpolation for divalent ions and to indicate the possibility of a convex-upward interpolation curve for the trivalent ions.

An interesting application of the ligand field component of the hydration energies is to analyze their effect on the oxidation-reduction potentials. The most numerous data (27) available apply to the reaction:

$$\mathrm{M^{2+}_{aq} + H^{+}_{aq} \longrightarrow M^{3+}_{aq} + {}^{1}/_{2}\, H_{2,g}} \qquad (19)$$

for which we may write:

$$\Delta F^0 = \Delta H_{H,}{}^{3+} - \Delta H_{H,}{}^{2+} + I_3 - T(S_{3+} - S_{2+}) - T\Delta S_{H^+ \rightarrow {}^1/_2 H_2} \qquad (20)$$

The heat of this reaction should vary through a transition series in about the same way as I_3, the third ionization potential of M; however, there are several other contributions to the total heat which obscure this relationship. The quantity $\delta H_{3+} - \delta H_{2+}$ contributes a driving force to the above reaction which varies erratically through a transition series. The other parts of the over-all heat vary monotonously with atomic number.

The contributions of the degeneracy of the ground levels to the entropy are no more than 2 e.u., and consequently they are negligible for our purposes. The vibrational entropy is probably affected by the configuration of the *d* shell, but we shall assume that the value of $S_{3+} - S_{2+}$ varies monotonously through a transition series.

Thus, if our assumptions are reasonable, the expected variation of ΔF^0, or of E^0, for reaction 19, through the transition series, should be given mainly by I_3 modified by $\delta H_{3+} - \delta H_{2+}$. In Figure 8, the measured oxidation potentials and the "corrected" oxidation potentials are plotted against atomic number. The "corrected" values are obtained by subtracting $\delta H_{3+} - \delta H_{2+}$ from the observed ΔF^0. Spectroscopic Dq values have been used to compute the δH. The resulting curve of corrected ΔF values looks very much like the

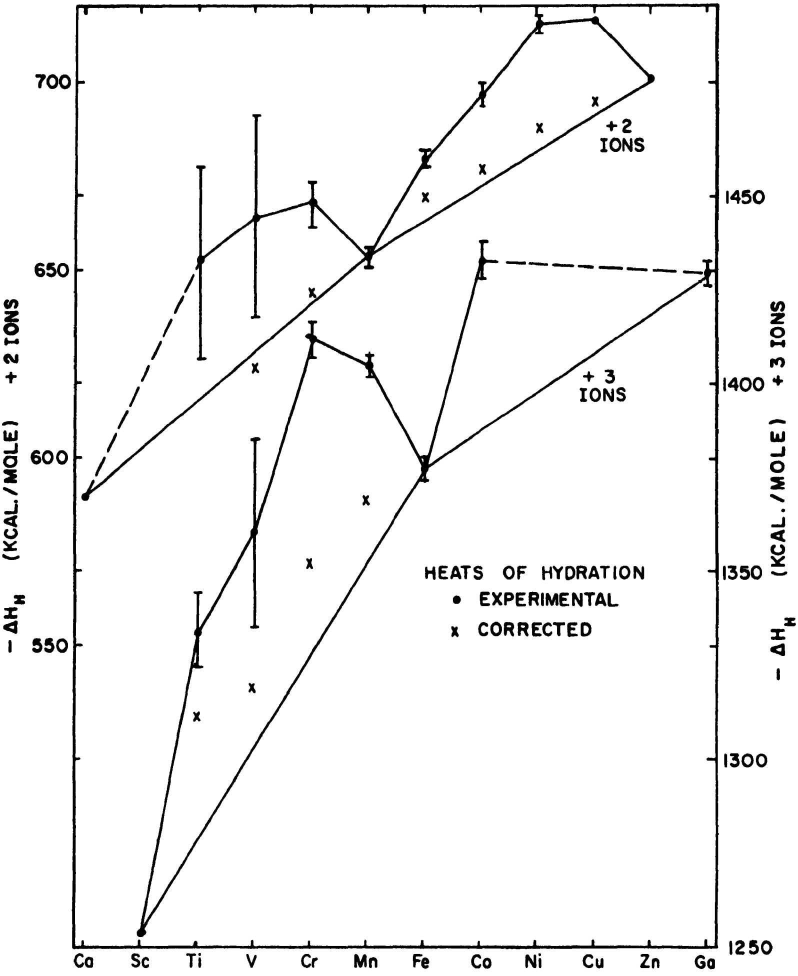

Fig. 7. Heats of hydration of transition metal ions. Values of δH derived from spectroscopic Dq's are subtracted from each value of $-\Delta H_H$ and form the "corrected" curve. The interpolation curve used in the text, the straight lines Ca–Mn–Zn or Sc–Fe–Ga, are also shown.

I_3 curve, also shown for comparison. The accuracy of the fit shows that the entropy change in the reaction is nearly the same for each element for which there is a measured value of ΔF^0. We conclude that

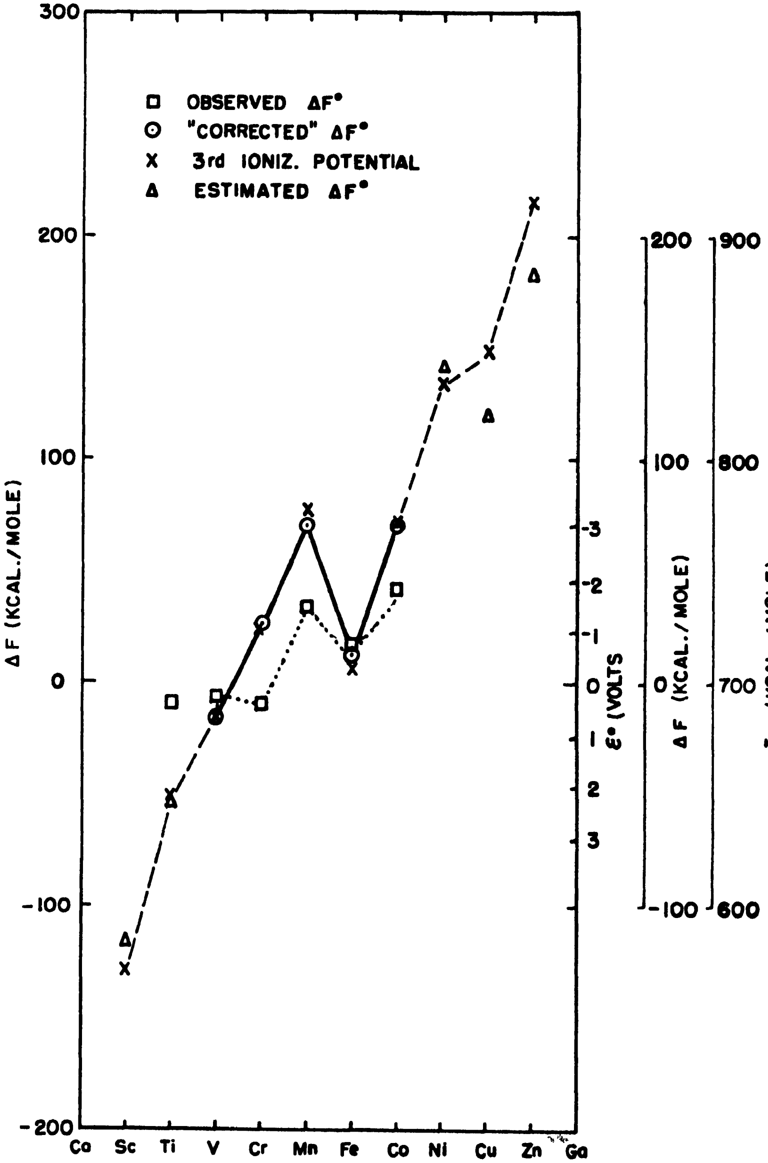

Fig. 8. The $M^{2+} \rightarrow M^{3+}$ oxidation potentials of the first transition series. The observed values, when corrected for ligand field effects, are seen to lie close to the I_3 values, also shown in the figure.

ligand field effects indeed produce the irregularities observed in the curve of oxidation potential versus atomic number.

In the case of $Ti^{2+} \rightarrow Ti^{3+} + e$, the estimated ligand field correction is very small and the corrected ΔF^0 does not lie near the I_3 curve. According to Latimer (27) the measured potential value may be too low. In order to obtain agreement with Figure 8, the E^0 value must be raised from 0.37 to 2.3 volts. This value would make Ti^{2+} almost as good a reducing agent as Mg metal. If our assumption, that the entropy change in this series of reactions varies slowly or not at all through the transition group, is radically wrong for Ti, the E^0 value would not have to be so high. Our results at least indicate that the present value is suspect and that further experimental work would be justified in this area.

If the same assumption about the entropy change is made for the reactions which are too energetic to be observed in solution, values of ΔF^0 or E^0 may be obtained for them. These values, including the ligand field effects, are also shown in Figure 8. The ligand field effect is responsible for making Cu^{3+} more stable than Ni^{3+}.

IV. Thermodynamic Properties of Coordination Complexes of Transition Metal Ions

A. THE FUNDAMENTAL GAS PHASE REACTION

Ligand field theory predicts that, just as with the crystalline inorganic compounds discussed above, the coordination complexes of the transition metal ions, except those with d^0, d^5, and d^{10} electronic configurations, should also show extra stabilization due to the splitting of the d orbitals into sets of different energy. The stabilization should appear as a more favorable, i.e., less positive or more negative, heat of formation of the complex relative to the value expected from the straight line or smooth curve drawn to give the best fit through the values for the d^0, d^5, and d^{10} ions.

The most fundamental heat of formation would be for the reaction in the gas phase between the ligand and the metal ion in its appropriate electronic valence state, i.e.,

$$M^{2+}{}_{g,v} + n\,L \rightleftharpoons (ML_n{}^{2+})_g \qquad \Delta H_{\mathrm{liq}} \qquad (21)$$

This is because only two heat (energy) terms are involved, in contrast to other reactions, as we shall see shortly. These terms are the ligand field stabilization present in the complex $(ML_n^{2+})_g$ and the $M^{2+}L$ interaction energy, which together go to make up the M^{2+}–L bond energy. There is no stabilization to take into account for the reactant metal ion, because in the gas phase the spherically symmetrical environment does not split the *d* orbitals. Reactions of this type cannot be studied experimentally, but considerable thermodynamic data are available for the formation of complexes in aqueous solution, where water molecules in the coordination shell are replaced by ligand groups. So it is essential first of all to establish the relationship between the change in heat content for this type of reaction and that for the fundamental reaction (eq. 21).

B. RELATIONSHIPS BETWEEN HEATS OF FORMATION OF HYDRATED IONS AND COMPLEX IONS IN THE GAS PHASE AND IN SOLUTION*

There is extensive crystallographic evidence that the fully hydrated ions of the transition metals under discussion contain six water molecules coordinated in the metal ion in an octahedral complex; and for simplicity in the equations which follow, we shall consider the complete replacement of these six water molecules by six monodentate ligand groups, i.e.:

$$[M(6\ H_2O)^{2+}]_{aq} + 6\ L_{aq} \rightleftharpoons [ML_6^{2+}]_{aq} + 6\ H_2O_{liq} \qquad \Delta H_c \qquad (22)$$

The individual reactions representing the stepwise replacement by mono-, bi-, and tridentate ligands, etc., can be treated in a similar way. The relation between ΔH_{lig} and ΔH_c, the change in heat content for the formation of the complex in solution, is provided, somewhat indirectly, by the reaction in which the gaseous ion is hydrated and dissolved in water to give the aquo-ion:

$$M^{2+}_{g,v} \xrightarrow{H_2O} [M(6\ H_2O)^{2+}]_{aq} \qquad \Delta H_H \qquad (23)$$

This is the over-all solvation reaction discussed above in Section III. Inspection shows that by addition of eqs. 22 and 23 we obtain the reaction between the gaseous ion and the ligand in solution giving the complex ion in solution:

$$M^{2+}_{g,v} + 6\ L_{aq} \rightleftharpoons [ML_6^{2+}]_{aq} \qquad \Delta H_L \qquad (24)$$

---

* In the present context the terms "hydrated ion" and "aquo-ion" will be used to denote the species $M(6\ H_2O)^{2+}$ in the gas phase and in aqueous solution, respectively.

This is analogous to reaction 23 for the formation of the aquo-ion, and it follows that the change in heat content, ΔH_L, is given by the equation:

$$\Delta H_L = \Delta H_H + \Delta H_c \tag{25}$$

It now remains to establish the connection between ΔH_H, ΔH_L, and the changes in heat content for the corresponding reactions in the gas phase, according to eq. 21. Let us denote these fundamental quantities for the bonding of six water molecules and six ligand groups by ΔH_{hyd} and ΔH_{com}, respectively. A consideration of the following Born-Haber cycle:

$$\begin{tikzcd}
M^{2+}_{g,v} + & 6\,H_2O_g \arrow[r, "\Delta H_{\mathrm{hyd}}"] & {[M(6\,H_2O)^{2+}]_g} \arrow[d, "\Delta H_{\mathrm{soln,\ hydrated\ ion}}"] \\
M^{2+}_{g,v} + \arrow[u] & 6\,H_2O_l \arrow[u, "6\lambda_{H_2O}"'] \arrow[r, "\Delta H_H"] & {[M(6\,H_2O)^{2+}]_{aq}}
\end{tikzcd}$$

shows that ΔH_H only differs from ΔH_{hyd} by the change in heat content accompanying the solution of the hydrated ion to give the aquo-ion, and by the latent heat of evaporation of the water molecules, λ_{H_2O} per mole, according to the equation:

$$\Delta H_H = \Delta H_{\mathrm{hyd}} + \Delta H_{\mathrm{soln,\ hydrated\ ion}} + 6\lambda_{H_2O} \tag{26}$$

Alternative ways of formulating this cycle have been adopted in various theoretical discussions (28). These involve evaporation of the water to leave a hole in the bulk of the solvent into which the metal ion or the hydrated ion is subsequently introduced; in such treatments the evaporation term is no longer $6\lambda_{H_2O}$. But for the present purposes the above cycle is to be preferred because it enables a very simple and direct comparison to be made between the bonding of water molecules and ligand groups in the first coordination shell.

The consideration of a corresponding cycle for the bonding of six ligand groups shows that ΔH_L only differs from ΔH_{com} by the change in heat content accompanying the solution of the complex ion, and by the heat of solution and latent heat of evaporation terms for the ligand, S_{lig} and λ_{lig} per mole, respectively, according to the equation:

$$\Delta H_L = \Delta H_{\mathrm{com}} + \Delta H_{\mathrm{soln,\ complex\ ion}} + 6(S_{\mathrm{lig}} + \lambda_{\mathrm{lig}}) \tag{27}$$

Hence, although ΔH_{hyd} and ΔH_{com} are the more fundamental quantities, the extent of the ligand field stabilization for the d^{1-4} and d^{6-9} ions can be assessed from the values of ΔH_H and ΔH_L because (*1*) the same λ_{H_2O} and $(S_{\text{lig}} + \lambda_{\text{lig}})$ terms hold for the d^0, d^5, and d^{10} ions and (*2*) to a first approximation, it can be assumed that the over-all dimensions of the hydrated ions, and of the complex ions, will not change significantly throughout a series—and therefore the heat of solution terms will also be the same. The validity of this assumption will be examined in a little more detail in Section IV-F.

While these equations have been developed for the reaction in which there is complete replacement of the water molecules in the hydrated ion by ligand groups, the partial replacement, in accord with the stepwise addition of ligands, can be treated in a similar way, as stated above. Equation 26 remains unaltered and ΔH_L is again calculated using eq. 25; but ΔH_L and ΔH_{com} now refer to the formation of complexes with both water molecules and ligand groups in the coordination shell. As a consequence, the equation corresponding to eq. 27 will contain the term $(6 - x)\ \lambda_{H_2O} + x(S_{\text{lig}} + \lambda_{\text{lig}})$, where x is the number of ligand groups, instead of $6(S_{\text{lig}} + \lambda_{\text{lig}})$, and the extra stabilization will be the result of a "mixed" ligand field.

It follows from eq. 27 that if S_{lig} and λ_{lig} are known, and if the heat of solution of the complex ion can be evaluated, then the more fundamental quantity ΔH_{com} for the gas phase reaction can be obtained. However, there is no satisfactory theory at present for the calculation of these heats of solution (see Section IV-E). On the other hand, a more elaborate Born-Haber cycle can be set up for the formation of a crystalline coordination compound, incorporating the standard heat of formation from the elements, which permits ΔH_{com} to be calculated (29). This method depends on an evaluation of the pseudo-lattice energy, which can be carried out using, for example, the Born or Born-Mayer equations. The pseudo-lattice energy in this cycle can be regarded as the term corresponding to the heat of solution of the complex ion in the cycle employed above. Values of ΔH_{com} have been obtained for the M^{2+} hexammines of several metals in the first transition series, but the method is of limited applicability because very few determinations of the heat of formation of crystalline coordination compounds have been made. Furthermore, with compounds having more complicated structures than the hexammines the evaluation of pseudo-lattice energies would be a far more difficult problem.

C. THE RESTRICTED NATURE AND THE LIMITATIONS OF THE DATA AVAILABLE FOR COMPLEXES IN SOLUTION

The criterion that data are also required for the d^0, d^5, and d^{10} ions, in order to estimate the ligand field stabilization energies of the d^{1-4} or d^{6-9} ions, restricts discussion to the M^{2+} complexes of Mn, Fe, Co, Ni, Cu, and Zn. There are too few data for corresponding M^{2+} complexes of Ca, Sc, . . . Mn, or for any M^{3+} complexes in the first series, or for either M^{2+} or M^{3+} complexes in the second and third series. Even with the M^{2+} complexes in the series Mn, Fe, . . . Zn, although combination with more than 500 ligands has been investigated, the vast majority belong to structural types which bond oxygen atoms, oxygen and nitrogen atoms, or entirely nitrogen atoms to the metal ion (30). The main correlation that can be looked for is thus one between stabilization energies and the number of bonded nitrogen atoms. At present the significant comparison of stabilization energies in complexes containing F^-, Br^-, NO_2^-, and CN^-, for example, rests upon the interpretation of optical spectra (10,31) and calculations based on lattice energies (see Sections II-B and II-C). The estimation of thermodynamic values for these ligands from solution data, and for the various classes of organic ligands containing S, P, and As, etc., is an important study for the future.

Furthermore, although there have been several thousand measurements of stability constants covering 500 ligands in combinations with ions in the series Mn^{2+} . . . Zn^{2+}, only for about seventy ligands have the constants been obtained for both Mn^{2+} and Zn^{2+} together with some for the ions in between (30). Moreover, in less than ten cases have the corresponding values of ΔH_c been determined, either from calorimetric measurements or from the variation of stability constants with temperature. This poses a serious problem, for ΔH_c is essential in the calculation of ΔH_L from eq. 25. However, in estimating stabilization energies, only the values of ΔH_L for the d^{6-9} ions relative to the values for the d^5 and d^{10} ions are required. The standard free energy changes can readily be calculated from the stability constants.* Therefore, provided that some generalization can be established for the entropy changes accompanying complex formation which is equally valid for all the ions in the series, relative values of ΔH_c, and hence the relative values of ΔH_L, can be calculated, and use can be made of the wealth of data for almost seventy ligands. Ideally, the generalization should be simple, to facilitate comparison, as well as a re-evaluation of the data and conclusions when the experimental values of ΔH_c become available.

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* The standard free energy change, ΔF^0, should strictly be calculated from the extrapolated value of the equilibrium (stability) constant at zero ionic strength. Very few studies of this kind have been made on the formation of complex ions. But for the present purpose only relative values are required, so, since the majority of the data for each ligand combining with the various metal ions were obtained

The standard entropy change for the formation of a complex ion in aqueous solution:

$$M^{2+}_{aq} + L_{aq} \rightleftharpoons ML_{aq}^{2+} \qquad \Delta S^0 \tag{28}$$

is given by the equation:

$$\Delta S^0 = \bar{S}^0_{ML^{2+}} - \bar{S}^0_{M^{2+}} - \bar{S}^0_L \tag{29}$$

where the terms on the right-hand side are the partial molal entropies of the complex, of the parent aquo-ion, and of the ligand in aqueous solution in that order. For a series of corresponding complexes of different metal ions, $\bar{S}^0_L$ will be a common term, and any differences in ΔS^0 will arise through the different values of $\bar{S}^0_{M^{2+}}$ and $\bar{S}^0_{ML^{2+}}$. However, a scrutiny of a number of ΔS values which can be calculated from data in the literature shows that, as a first approximation, ΔS for the formation of a complex in the series Mn^{2+} . . . Zn^{2+} is independent of the particular metal ion. In Table XI, ΔS values, 77 in all, have been gathered together for ten ligands. Within the several sets of corresponding complexes, the ΔS values for 48 complexes span only 3 e.u. and those for 59 complexes span 6 e.u. Thus, taking the latter figures, relative values of ΔH_c can be obtained from the values of ΔF in three-fourths of the cases with an uncertainty of ±1 kcal./mole (the $T\Delta S$ span being 2 kcal./mole). It may be noted that the majority of experimental values for ΔH_c are subject to at least the

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under identical ionic strength conditions, no serious error will result. For this reason values of the free energy change calculated from $-RT$ ln (stability constant) will be simply referred to as ΔF, and the entropy change, $(\Delta F - \Delta H_c)/T$, as ΔS. Under the same conditions of ionic strength, the values of ΔS for a series of corresponding complexes will show the same variation as the values for the standard entropy change, ΔS^0.

In quite a number of cases, too, the stability constants have been measured at 20 or 30°C., for example, rather than at the standard temperature of 25°C.; but, again, as far as the relative ΔF values are concerned, any difference from the values appropriate to 25°C. will be very small, and therefore negligible.

TABLE XI
Entropy Changes for the Formation of Various Complexes of Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}

Ligand	No. of ligands	Entropy change, e.u.						Ref.[a]
		Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	
Acetylacetone	1	+13		+13	+12	+28	+13	I *120*, 4
	2	+15		+17	+7	+38	+18	
8-Hydroxy-2-methylquinoline[b]	2	+42		+50	+46	+51	+51	I *350*, 1,2,3
8-Hydroxy-4-methylquinoline[b]	2	+32		+24	+18		+28	I *351*, 1
Ethylenediamine-*N,N,N'N'*-tetra-acetic acid	1	+41		+58	+55	+55	+55	I *362*, 3; c
Imidazole	1					0	−3	I *26*, 3,4
	2					−1	−1	
	3					−4	+2	
	4					−9	+2	
Ammonia	1			+2	+2	+1	−1	II *24*, 10
	2			+3	+2	−1	−1	
	3			0	−1	−6	−1	
	4			−4	−6	−15	−3	
	5			−10	−13			
	6			−21	−24			
Ethylenediamine	1				+2	+5	+9	I *12*, 7,19; d
	2				+5	+5	+14	
	3				−4		+23	
cis-1,2-Cyclohexanediamine	1				+7	+10	+9	d
	2				+13	+13	+19	
trans-1,2-Cyclohexanediamine	1				+8	+5	+12	d
	2				+13	+8	+19	
2,2'-Diaminodiethylamine	1	+4	0	+9	+11	+6	+15	I *86*, 2

[a] For I *120*, 4, etc., see ref. 30.

[b] Measurements made on dioxane–water solutions.

[c] R. G. Charles, *J. Am. Chem. Soc.*, *76*, 5854 (1954).

[d] C. R. Bertsch, W. C. Fernelius, and B. P. Block, *J. Phys. Chem.*, *62*, 444 (1958).

same uncertainty. This very simple generalization regarding the constancy of ΔS can be expected to give equally reliable relative values of ΔH_c for the other ligands, where no experimental values are available, because those in Table XI are fully representative of the various structural types. Undoubtedly there will be exceptions, as there are in the table, but some of these may be due to experimental error, since they seem to occur haphazardly. Insofar as the generalization does appear to be widely applicable, a well-authenticated exception with a very discrepant ΔS value would be an indication that some specific interaction is present.

In a previous discussion of stabilization energies the relative values of ΔH_c were calculated according to a different generalization, namely, that in the series Mn^{2+} . . . Zn^{2+} the partial molal entropy of a complex ion is independent of the particular metal (32). We shall find that the present calculations lead to the same broad conclusions regarding the influence of structural factors on the magnitude of stabilization energies, since the corrections that were applied to the ΔF values were small with the result that both sets of relative values for ΔH_c show the same trends.

The calculation procedure used previously depended on values adopted for the partial molal entropies of the Co^{2+} and Ni^{2+} aquo-ions (33). Following Latimer (27), the values of -37.1 and -38.1 e.u., respectively, obtained from experimental data (22), were disregarded; instead, values were estimated using Powell and Latimer's empirical equation, taking 0.72 and 0.71 A. for the ionic radii (34). The results were -24 and -25 e.u. for Co^{2+} and Ni^{2+}, respectively, compared to the experimental values of -23.6 and -25.4 e.u. for the Cu^{2+} and Zn^{2+} aquo-ions (22). The close correspondence of these four values, in conjunction with the similar values of ΔS for the formation of many Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} complexes, thus suggested, as can be seen from eq. 29, that the partial molal entropy of a complex ion in the series is independent of the metal. But there is no experimental justification for disregarding the values of -37.1 and -38.1 e.u. for CO^{2+} and Ni^{2+}; moreover, the approximate constancy of the ΔS values has been well established through many independent experiments, and has therefore been chosen as the basis for calculations. An added advantage is that the calculations are now simpler, for the relative values of ΔH_c are given directly by the relative values of ΔF. If the experimental $\bar{S}^0$ values for the Co^{2+} and Ni^{2+} aquo-ions are adopted, the $\bar{S}^0$ values for their complexes differ appreciably from those for the Cu^{2+} and Zn^{2+} complexes, and reference to eq. 29 shows that for ΔS (and ΔS^0, see footnote, page 424) to remain approximately constant the variation in the partial molal entropies of the complex ions must follow closely the variations in the values for the aquo-ions.*

D. CALCULATIONS

1. The Typical Variation of ΔH_L with Atomic Number for the M^{2+} Complexes of Mn, Fe, Co, Ni, Cu, and Zn

The values of the heat of solvation ΔH_H, recalculated from the most recent data in Section III, have been used in the calculations. In view of the uncertainties of ±3, ±3, and ±2 kcal./mole for Mn^{2+}, Co^{2+}, and Ni^{2+}, all the values have been rounded off to the nearest whole number, giving 654, 680, 697, 716, 717, and 701 kcal./mole, respectively, for $Mn^{2+} \ldots Zn^{2+}$. Relative to Mn^{2+}, the increments in ΔH_H are thus 26, 43, 62, 63, and 47 kcal./mole for $Fe^{2+} \ldots Zn^{2+}$. Values of ΔH_c relative to the value for Mn^{2+} have been obtained by the procedure developed in Section IV-C and a typical calculation is illustrated in lines 1, 2, and 3 of Table XII for the trisethylenediamine

TABLE XII

The Calculation of the Values of ΔH_L, Relative to the Value for Mn^{2+}, for $Fe^{2+} \ldots Zn^{2+}$, and the Calculation of the Stabilization Energies, δH, for $Fe^{2+} \ldots Cu^{2+}$, in the Case of the Trisethylenediamine Complexes (30: I, *12*, 7, 11, 19)

	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
1. Log (stability constant)	5.66	9.52	13.82	18.61	18.7	12.09
2. ΔF, kcal./mole	7.9	13.2	19.2	25.9	26.0	16.8
3. ΔF (i.e., ΔH_c) relative to value for Mn^{2+}		5	11	18	18	9
4. ΔH_H relative to value for Mn^{2+}		26	43	62	63	47
5. ΔH_L relative to value for Mn^{2+}		31	54	80	81	56
6. $[(n-5)/5]E_r$		11	22	34	45	
7. δH		20	32	46	36	

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* *Note added in proof:* Since the preparation of this article L. A. K. Staveley and T. Randall have published new calculations giving −22 and −23 e.u. for the partial molal entropies of the Co^{2+} and Ni^{2+} aquo-ions, respectively (see "Ions of the Transition Elements," *Discussions Faraday Soc., No. 26*, 157 (1958)). This publication also includes several other papers and many discussion comments on the present subject, e.g., by J. W. Linnett, C. K. Jørgensen, D. P. Craig and E. A. Magnusson, R. J. P. Williams, N. S. Hush, etc.

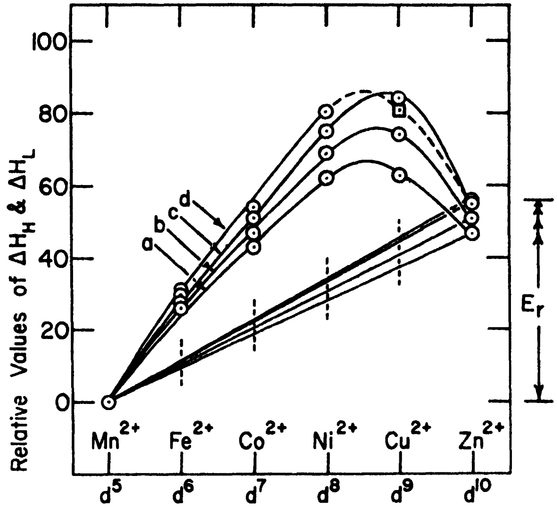

Fig. 9. The values of ΔH_H (*a*) and ΔH_L for the mono-, bis-, and trisethylenediamine complexes (*b*, *c*, and *d*, respectively) of Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} relative to the corresponding values for Mn^{2+}, plotted against atomic number.

complexes. Lines 1 and 2 give log (stability constant) and ΔF, respectively. Line 3 gives the values of ΔF relative to the value for Mn^{2+}, which, assuming that ΔS is the same for all the complexes, are equivalent to the relative values of ΔH_c. The relative values of ΔH_L have then been obtained by adding these values to the corresponding relative values of ΔH_H according to eq. 25, as shown in lines 4 and 5.

The plot of ΔH_H against atomic number for Mn^{2+} . . . Zn^{2+} gives the humped curve rising to about 35 kcal./mole above the line joining the values for Mn^{2+} and Zn^{2+} (Fig. 7). Since the values of ΔH_c relative to the value for Mn^{2+} show a smaller variation, amounting at the most to about 20 kcal./mole in only a very few cases, the plots of ΔH_L against atomic number are quite similar to those for ΔH_H. Plots typical of the entire range of values are given in Figure 9 which includes the relative values of ΔH_H for comparison, and ΔH_L for the mono-, bis-, and trisethylenediamine complexes. As the water molecules coordinated to the metal ion are successively replaced by up to four nitrogen atoms, the maximum in the curve moves to the right, but further coordination of the cupric ion results in very weak complexes, so the curve for six nitrogen atoms (three ethylenediamine groups) has the maximum displaced toward the left. Throughout the replacement, the value of ΔH_L for Zn^{2+} relative to Mn^{2+} gets progressively larger, as shown by the increased slope of the line joining the respective points. The difference between these values for the d^{10} and d^5 ions, which is independent of d orbital splitting, may be called a "transition series contraction energy," since the greater values for the d^{10} ion relative to the d^5 ion accompany a decrease in ionic radius. The "lanthanide contraction" is a related phenomenon. However, in the discussion of lattice energies of d^0, d^5, and d^{10} compounds in Section II, we have seen that repulsion energies also play a significant role in determining some of the values. The symbol E_r, with the appropriate qualification, was used there to denote the difference between values for either the d^5 and d^0 or d^{10} and d^5 ions, but in the following discussion of coordination complexes, where the data are more limited, it will be used without qualification to signify the difference for Zn^{2+} and Mn^{2+} complexes.

The change in position of the curves in Figure 9, arising from the increased heats of formation of the Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} complexes relative to those of Mn^{2+} and Zn^{2+}, is attributable to the greater splitting between the t_{2g} and e_g orbitals in the ligand field containing nitrogen atoms, and stabilization energies for the d^{6-9} ions can be obtained in the following manner.

2. *Stabilization Energies for Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} Complexes*

Thermodynamic stabilization energies, δH, can be most simply defined as the increment between the ΔH_L values for the Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} complexes and the interpolated values given vertically below on the line joining the points for Mn^{2+} and Zn^{2+}. This is a purely empirical definition, and the δH values so calculated would only have physical significance, if, in the absence of the ligand field, the interpolated values of ΔH_L are a truly linear function of atomic number between Mn and Zn. As a first approximation, this is probably not far from the truth, in view of the reasonable linearity found in the case of the lattice energies of the M^{2+} compounds (Section II). Later, when we come to compare the thermodynamic stabilization energies for the complexes with those calculated from optical data, we shall be in a better position to judge.

TABLE XIII
Data for Complexes of Mn^{2+} ..... Zn^{2+} with Inorganic Anions, Carboxylic Acids, β-Diketones, etc.

Ligand	No. of ligands	E_r (Mn–Zn)	δH, kcal./mole				Ref.[a]
			Fe	Co	Ni	Cu	
H_2O (i.e., the aquo-ions)	6	47	17	24	34	25	Calculations in Section III
Cl^-	1		≤ values for H_2O				II *52*, 83a, 89, 109, 110; *53*, 20, 29, 99, 103
SO_4^{2-}	1		≤ values for H_2O				II *44*, 92, 94, 98, 106
$S_2O_3^{2-}$	1		≤ values for H_2O				II *42*, 4, 6, 15, 26
OH^-	1	49	18	22	33	28	II *2*, 66, 68; *3*, 3, 10
Oxalic acid	1	48		25	35	28	I *5*, 5
	2	50	22	25	34	30	I, *5*, 7, 14, 15, 24
Malonic acid	1	48		25	34	28	I *25*, 2, 7
Salicylaldehyde[b]	1	48	17	25	35	30	I *237*, 1, 2
	2	49	17	25	36	33	
Acetylacetone	1	48	17	26	37	31	I *120*, 1, 4
	2	49	18	26	37	35	
Dibenzoylmethane[b]	1	48	19	25	35	30	I *433*, 1, 3
	2	50	21	26	36	33	
Benzoylacetone[b]	1	47	19	26	36	31	App. I, 91
	2	47	22	28	38	36	
Benzoyl-2-furoyl-methane[b]	1	47	19	26	36		App. I, 90, 91
	2	47	22	28	38		
2-Thenoyl-2-furoyl-methane[b]	1	48	18	25	35		I *379*, 1
	2	49	21	26	37		
Benzoyl trifluoro-acetone[b]	2	46	20	28	38	33	App. I, 90, 91
Tetracycline	1	48	17	25	35	30	c
Terramycin	1	47	19	25	36	29	I *462*, 1
Aureomycin	1	47	19	25		29	I *463*, 1
2-Nitroso-1-naphthol[b]	1	49			38		I *346*, 1
	2	51			41		

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[a] For II *52*, 83a, etc., see ref. 30. App. I, 90, etc., indicate references in Appendix I of *Chemistry of Metal Chelate Compounds* by A. E. Martell and M. Calvin, Prentice-Hall, New York, 1952.

[b] Measurements made on dioxane–water solutions.

[c] A. Albert and C. W. Rees, *Nature, 177*, 433 (1956).

TABLE XIV
Data for Complexes of $Mn^{2+} \ldots Zn^{2+}$ with α-Amino- and α-Iminomonocarboxylic Acids, etc.

Ligand	No. of ligands	E_r (Mn–Zn)	δH, kcal./mole				Ref.[a]
			Fe	Co	Ni	Cu	
Glycine	1	50	18	26	36	30	I *20*, 15, 16
	2	52	19	27	38	34	
Glycylglycine	1	49		25	35	28	I *96*, 1
Alanine	1	50		25	36	30	I *45*, 2, 7, 8
	2	52	18	26	37	33	
Valine	1	50		25		30	I *150*, 2, 3
	2	52	17	26		33	
Leucine	1	50		25		30	I *220*, 1
	2	52		26		33	
Aspartic acid	1	50		26	37	30	I *92*, 3, 5
Proline	2	53	19	27	38	37	I *140*, 1
Tryptophan	2	53	19	27	37	36	App. I, 47
Di(2-hydroxyethyl)-aminoacetic acid	1	50	18	26	37	30	I *223*, 1
	2	51	19	28	38	33	
Quinoline-8-carboxylic acid[b]	1	48		23	33	30	I *348*, 1, 2
Histidine	1	51		27		31	I *207*, 3, 4
	2	54	17	29	41	34	
Cysteine	1	54	18	28			I *53*, 1, 2

[a] I *20*, 15, etc., see ref. 30; for App. I, 47, see footnote a of Table XIII.

[b] Measurements made on dioxane–water solutions.

Reference to Figure 9 shows that δH for the complex ion with n d electrons, $5 < n < 10$, can be obtained from the expression

$$\delta H = (\Delta H_L)_{d^n} - [(n - 5)/5]E_r \qquad (30)$$

where $(\Delta H_L)_{d^n}$ is the value of ΔH_L for the d^n ion relative to the value for Mn^{2+}. Typical calculations are given in lines 6 and 7 of Table XII for the trisethylenediamine complexes.

The acquisition of δH values for as many ligands as possible has been greatly facilitated by the recent publication on stability constants by J. Bjerrum, G. Schwarzenbach, and L. G. Sillén (30). These compilations have enabled the earlier survey (32), which covered 23 complexes of 18 ligands, to be extended to 94 complexes of 67 ligands. References to the original papers, containing the stability constants from which the δH values in Tables XIII–XVIII have

TABLE XV

Data for Complexes of Mn^{2+} .... Zn^{2+} with α-Iminodicarboxylic Acids, etc.

Ligand	No. of ligands	E_r (Mn–Zn)	δH, kcal./mole				Ref.[a]
			Fe	Co	Ni	Cu	
Methyliminodiacetic acid	1	50	18	26	37	31	I *142*, 1, 2
	2	53	18	28	39	32	
Cyanomethyliminodiacetic acid	1	50		26	36	28	I *206*, 1
	2	52		28	39	30	
N-(Carbamoylmethyl)iminodiacetic acid	1	50		26	36	29	I *212*, 1
	2	50		27	38	31	
2-Methoxyethyliminodiacetic acid	1	51	18	26	36	31	I *269*, 1
	2	51	18	27	38	31	
2-Methylthioethyliminodiacetic acid	1	51	19	28	38	32	I *270*, 1
	2	52	19	28	39	32	
2-Ethoxycarbonylaminoethyliminodiacetic acid	1	50		26	36	31	I *325*, 1
	2	52		28	40	32	
Phenyliminodiacetic acid	1	49	17	25	36	31	I *356*, 2
3,3-Dimethylbutyliminodiacetic acid	1	50		26	36	31	I *365*, 1
	2	53		27	38	32	
2-Di(carboxymethyl)aminoethyltrimethylammonium cation	1	50		27	36	30	I *327*, 1
Ethylenediamine-*N*,*N*-diacetic acid	1	53	18	26	38	32	I *217*, 1
Ethylenediamine-*N*,*N*′-dipropionic acid	1	53	19	27	38	37	I *307*, 1
2-Mercaptoethyliminodiacetic acid	1	56	18	28	32		I *230*, 1

[a] For I *142*, 1, etc., see ref. 30.

been calculated, are quoted from this source in almost all cases. Each ligand has a serial number, and, taking ethylenediamine as an example, the reference for the data used in Table XII is I *12*, 7, 11, 19, indicating that ethylenediamine is ligand number 12 in Part I and the values of log K chosen for the complexes of Mn^{2+} . . . Zn^{2+} are contained there in footnote references 7, 11, and 19. In Tables XIII–XVIII the ligands have been grouped together as far as possible ac-

TABLE XVI

Data for Complexes of $\mathrm{Mn}^{2+} \ldots \mathrm{Zn}^{2+}$ with α-Iminotri- and α-Iminotetracarboxylic Acids, etc.

Ligand	No. of ligands	E_r (Mn–Zn)	δH, kcal./mole				Ref.[a]
			Fe	Co	Ni	Cu	
Nitrilotriacetic acid	1	51	18	27	36	29	I *209*, 3
N'-(2-Hydroxyethyl)-ethylenediamine-*N*,*N*,*N'*-triacetic acid	1	52	17	27	40	30	I *364*, 1
Ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid	1	51	17	27	38	29	I *362*, 2, 4, 5
1,2-Diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetraacetic acid	1	50		26		26	I *420*, 1
Ethylenediamine-*N*,*N*,*N'*,*N'*-tetrapropionic acid	1	51	18	27	38	37	I *425*, 1
2,2'-Bis[di(carboxyethyl)amino]diethyl ether	1	50	18			29	I *396*, 1
2,2'-Bis[di(carboxymethyl)amino]diethyl sulfide	1	52	19		38	30	I *398*, 1

[a] For I *209*, 3, etc., see ref. 30.

cording to their structural types. Table XIII contains a few inorganic but mainly organic ligands in which the bonding atoms are solely oxygen. Tables XIV–XVI contain amino and imino mono-, di-, tri-, and tetracarboxylic acids, in which the bonding atoms are both oxygen and nitrogen. Table XVII contains miscellaneous ligands of this general type, and Table XVIII polydentate amines in which the bonding atoms are entirely nitrogen.

In view of the general tendency for the transition metal ions to form octahedral complexes, when there are insufficient ligand groups to coordinate the metal ion completely it will be assumed that water molecules make up the deficiency. With dimethylglyoxime monomethyl ether the values obtained are so much out of keeping with all those for complexes containing otherwise identical bonding atoms that this is probably the only ligand which preferentially forms square

TABLE XVII

Data for Complexes of $Mn^{2+} \ldots Zn^{2+}$ with 8-Hydroxyquinolines and Other Ligands Having Similar Donor Groups

Ligand	No. of ligands	E_r (Mn–Zn)	δH, kcal./mole				Ref.[a]
			Fe	Co	Ni	Cu	
8-Hydroxyquinoline-5-sulfonic acid	1	50	19	27	37	31	I *328*, 2
	2	52	21	29	40	37	
8-Hydroxy-2-methylquinoline[b]	1	50		26	35	30	I *350*, 1, 2, 3
	2	54		27	35	33	
8-Hydroxy-4-methylquinoline[b]	1	50		26	36		I *351*, 1
	2	54		27	39		
4-Hydroxypteridine	1	49	17	25	36	27	I *191*, 1, 2
Pteroylglutamic acid	2	49	19	26	37	26	I *454*, 1
Riboflavin	1	50	21	24	33		I *450*, 1
2-(*o*-Hydroxyphenyl)-benzothiazole[b]	1	50	21	29			I *414*, 1, 2
5-Hydroxy-4-*o*-hydroxyphenylazo-3-methyl-1-phenylpyrazole[b]	1	51		28	37	34	I *440*, 1
1-(5-Chloro-2-hydroxyphenylazo)-2-naphthol[b]	1	51	21	34	38	34	I *443*, 1

[a] For I *328*, 2, etc., see ref. 30.

[b] Measurements made on dioxane–water solutions.

planar complexes—like that well established for the Ni^{2+} complex of the parent compound. Several isomers are possible for some intermediary complexes, but there is no evidence of irregularities in the present data to suggest that at a certain stage an energetically favored intermediate is formed.

An examination of Tables XIV–XVI and XVIII reveals a progressive increase in both δH and E_r as water in the coordination shell is replaced by nitrogen-containing groups. Average values are brought together in Table XIX for ligands that furnish an identical number of aliphatic bonding N atoms. For example, one bonding N atom is provided by both aminomonocarboxylic acids and iminodicarboxylic acids; two bonding N atoms are provided by one aliphatic diamine, by two aminomonocarboxylic acids, and by two iminodicarboxylic acids, etc. Amines with nitrogen conjugated in aromatic structures have not been included, nor have the iminotri-

TABLE XVIII

Data for Complexes of Mn^{2+} ... Zn^{2+} with Polydentate Amines, etc.

Ligand	No. of ligands	E_r (Mn–Zn)	δH, kcal./mole				Ref.[a]
			Fe	Co	Ni	Cu	
Ethylenediamine	1	51	18	27	38	33	I, *12*, 7, 11, 19
	2	55	19	29	42	40	
	3	56	20	32	46	36	
2,2′-Diaminodiethylamine	1	54	18	27	38	36	I *86*, 1, 2, 3
	2	57	20	31	45	36	
2,2′,2″-Triaminotriethylamine	1	59	18	28	38	32	I *188*, 1
N,*N*′-Di-(2-aminoethyl)-ethylenediamine	1	56	19	29	40	39	I *189*, 3
Tetraethylenepentamine	1	58			42	39	d
N,*N*,*N*′,*N*′-Tetrakis-(2-aminoethyl)-ethylenediamine	1	56	18	30	41	36	I *344*, 1
2,2′-Dipyridyl	3	57	30	32	44	33	I *337*, 3, 4, 8, 9; c
1,10-Phenanthroline	3	60	33		41	29	I *338*, 2, 5, 10, 11, 14, 15
2-*p*-Dimethylaminophenylazopyridine	1	49		27	37	29	I *405*, 1
Dimethylglyoxime *O*-monomethyl ether[d]	1	49		28	33	29	I *144*, 1, 2
	2	51		31	32	28	

[a] For I *12*, 7, etc., see ref. 30.

[b] C. N. Reilly and J. H. Holloway, *J. Am. Chem. Soc.*, *80*, 2917 (1958).

[c] G. F. Wells, Ph.D. Thesis, Leeds University, England, 1953.

[d] Measurements made on dioxane–water solutions.

and iminotetracarboxylic acids in which steric effects may play a part. These ligands and those in Table XVII will be discussed separately later.

It can be seen that there is very close agreement between the δH and E_r values for complexes containing the same number of aliphatic bonding N atoms, and in Figure 10 weighted mean values have been plotted against the number of bonding N atoms in the case of E_r, and δH for Co^{2+}, Ni^{2+}, and Cu^{2+}. The variations of δH for Co^{2+} and

TABLE XIX
Correlation between Stabilization Energies for the Complexes of Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} and the Number of Aliphatic Bonded Nitrogen Atoms

Ligand	Max. no. of examples	No. of bonded N atoms	E_r (Mn–Zn)	δH, kcal./mole			
				Fe	Co	Ni	Cu
Aminomonocarboxylic acid	7	1	49.9 ± 0.2	18.0	25.4 ± 0.5	36.2 ± 0.6	29.7 ± 0.5
Iminodicarboxylic acids	9	1	50.1 ± 0.6	18.0 ± 0.5	26.2 ± 0.6	36.3 ± 0.5	30.4 ± 1.0
Aliphatic polydentate amines	1	2	51	18	27	38	33
Aminomonocarboxylic acids	7	2	52.1 ± 0.5	18.5 ± 0.7	26.7 ± 0.6	37.6 ± 0.5	34.1 ± 1.3
Iminodicarboxylic acids	7	2	51.9 ± 0.8	18.3 ± 0.4	27.6 ± 0.5	38.7 ± 0.6	31.4 ± 0.7
Aliphatic polydentate amines	1	3	54	18	27	38	36
	3	4	56.7 ± 1.6	18.7 ± 0.4	28.7 ± 0.4	40.0 ± 1.3	37 ± 3
	1	5	58			42	39
	3	6	56.3 ± 0.4	19.3 ± 0.9	31 ± 1	44 ± 2	36

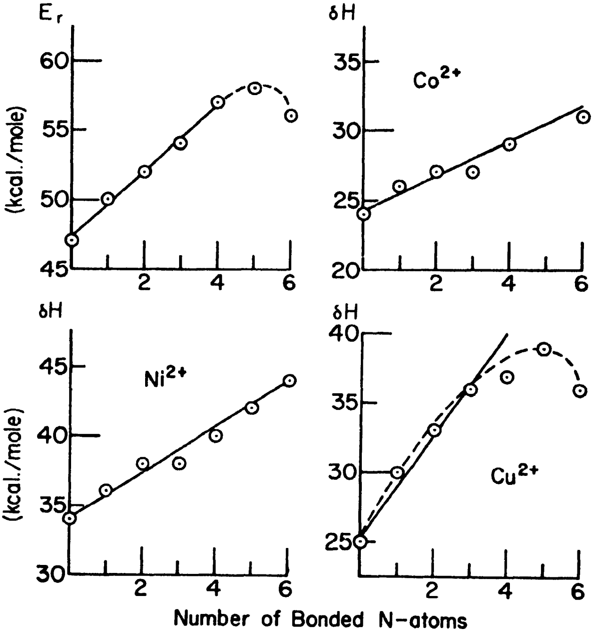
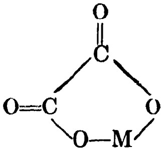


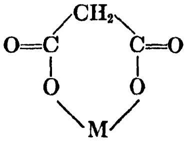
Fig. 10. E_r and δH for Co^{2+}, Ni^{2+}, and Cu^{2+} plotted against the number of bonded N atoms for complexes with aliphatic polydentate amines, aminomonocarboxylic acids, and iminodicarboxylic acids.

Ni^{2+} are approximately linear over the whole range; E_r is linear up to four N atoms; and the points for Cu^{2+}, which shows the greatest increase in δH, are best fitted by a smooth curve. E_r and δH for Cu^{2+} decrease again when more than four N atoms are bonded, an effect foreshadowed in the much smaller stability constants for the addition of the fifth and sixth ligand groups. As can be seen in Table XIX, δH for Fe^{2+} shows only a very slight increase, amounting to about 1 kcal./mole over the entire range, whereas the values for Co^{2+}, Ni^{2+}, and Cu^{2+} span 7, 10, and 14 kcal./mole, respectively. Although δH for Cu^{2+} shows the greatest increase, the stabilization energies for corresponding complexes follow the order:

$$Ni^{2+} > Cu^{2+} > Co^{2+} >> Fe^{2+} \qquad (31)$$

This simple correlation between δH and the number of bonded N atoms for 22 ligands, which, although possessing the same coordination groups nevertheless differ a great deal in gross chemical structure, is evidence that the stabilization energies are determined almost entirely by the atoms directly bonded to the central metal ion. Moreover, since the amino- and iminocarboxylic acids give the same stabilization energies as aliphatic amines donating an identical number of nitrogen atoms, it would appear that the oxygen atom of a carboxylate group and of a water molecule make very similar contributions to the ligand field. This is borne out by the values in Table XIII for coordination with one oxalate or malonate ion. With these ligands, even though two carboxylate groups are bonded giving five- and six-membered chelate rings (I and II, respectively), the values of E_r and δH for Co^{2+} and Ni^{2+} only exceed the values for water by 1 kcal./mole and the value of δH for Cu^{2+}, which is the most susceptible to ligand replacement, is only increased by 3 kcal./mole, about half the increment for one bonded N atom.


(I)

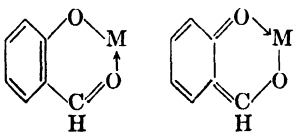

(II)

The same generalization has been found to hold in the case of optical spectra of complexes of transition metal ions, the frequencies for maximum absorption in the visible or near infrared being almost unequivocally determined by the atoms in the first coordination shell (10). Furthermore, the additive effect of bonded N atoms has its counterpart in the "average environment" rule (31). If the ligands are arranged in a spectrochemical series according to the extent to which they shift the band maxima, then, independent of the particular metal, the following order is obtained for the directly bonded atoms:

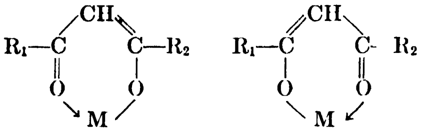
$$N > O > F > Cl > Br$$

If several different ligands are bonded, as in $Ni(NH_3)_4(H_2O)_2{}^{2+}$, the band maxima correspond to a position in the series given by the average of the positions for the single ligands. It is only to be expected that thermodynamic and optical data lead to these same conclusions because a common energy parameter is involved, the splitting of the *d* orbitals in the ligand field (see Section IV-E).

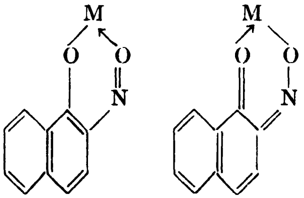
Turning now to the data in Table XIII, it is apparent that a correlation, similar to that for the bonding of nitrogen, holds for a group of more complicated organic ligands in which the bonding atoms are entirely oxygen. In these complexes chelate rings are formed for which resonating structures can be written, viz., salicylaldehyde (III), β-diketones (IV), tetracyclines,* and 2-nitroso-1-naphthol (V). Aver-



(III)

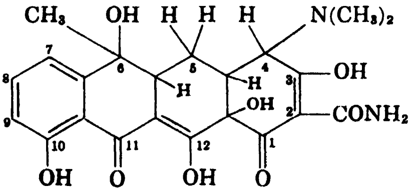


(IV)



(V)

* Tetracycline has the structure



Tetramycin and aureomycin are the 5-OH- and 7-Cl-substituted derivatives, respectively. With these very complicated polyfunctional ligands it has been assumed that bonding of the metal ion occurs via one of the pairs of adjacent OH and carbonyl oxygen groups, i.e., at positions 10 and 11, 11 and 12, or possibly 12 and 1; but an alternative site is afforded by the OH and $N(CH_3)_2$ groups at positions 3 and 4, respectively. The values of δH for the tetracyclines in Table XIII and those for ligands bonding one N atom (e.g., 8-hydroxyquinolines in Table XVII and amino- and iminoacetic acids in Table XIX) are so close that no distinction

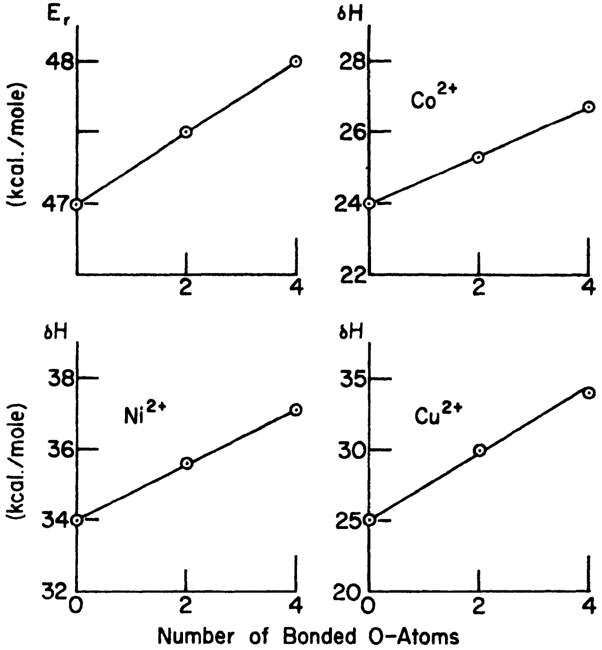


Fig. 11. E_r and δH for Co^{2+}, Ni^{2+}, and Cu^{2+} plotted against the number of bonded O atoms for complexes with salicylaldehyde, β-diketones, and tetracyclines.

age values of E_r and δH are brought together in Table XX. Corresponding values for salicylaldehyde, the β-diketones, and the tetracyclines are in such close agreement as to justify plotting weighted mean values against the number of bonded ligand oxygen atoms as shown in Figure 11. Linear relationships are again obtained, and although the values cover a smaller range than those for N atom bonding (Fig. 10), it is immediately apparent that oxygen in these complexes exerts a stronger ligand field effect than it does in a water molecule or a carboxylate ion. For the bonding of four O atoms, the increase in E_r is about the same as that produced by one N atom, while the increases in δH for Co^{2+}, Ni^{2+}, and Cu^{2+} approximate those for two N atoms. The increase in δH for Fe^{2+} is again quite small, but

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can be made. The values of E_r for the tetracyclines, however, are in better agreement with those for salicyaldehyde and the β-diketones (see Table XIII), and they have accordingly been grouped together. More direct evidence to identify the bonding site in the tetracyclines is very desirable.

does not fit into this general pattern, being greater than that observed with N atom bonding. This may be a genuine difference, although the stability constants could be in error because of partial oxidation. The stabilization energies for corresponding complexes, however, follow the same order as before:

$$Ni^{2+} > Cu^{2+} > Co^{2+} >> Fe^{2+}$$

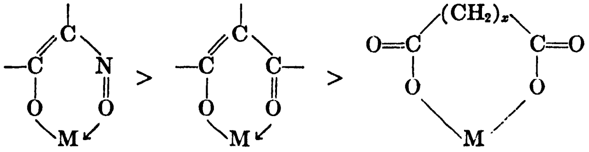
In the case of the nitrogen-bonding ligands discussed above, all the determinations of stability constants were made in aqueous solutions, but with these oxygen-bonding ligands only the data for acetylacetone, tetracycline, and the two derivatives of tetracycline refer to aqueous solutions; the data for salicylaldehyde and the five other β-diketones were obtained from measurements on dioxane–water solutions. Nevertheless, the very close agreement between the E_r and δH values for all these oxygen-bonding ligands provides good evidence that this particular change in the nature of the solvent has very little effect. This is to be expected, since water is a more potent ligand than dioxane, and so in the dioxane–water mixtures it is highly likely that the remaining coordination positions will still be occupied by water molecules. Measurements with several other large organic ligands were also carried out in this mixed solvent as indicated in the tables, but in view of the above agreement it is improbable that the presence of dioxane affects the values.

Another interesting aspect of the similarity between the values for salicylaldehyde, the β-diketones, and the tetracyclines is that, although once the chelate ring is formed it contains the same atoms in the same order, the bonding oxygen atoms are originally present in phenolic and enolic hydroxyl groups and in aldehydic and ketonic carbonyl groups. The E_r and δH values thus do not reflect differences in chemical reactivity that characterize the bonding groups in the parent ligands. On the other hand, with 2-nitroso-1-naphthol, where the chelate ring has —N= in place of —CH= (see III–V). the increments in E_r and δH for Ni^{2+} (the only values available) are twice as great. For the complexes containing two ligands, i.e., four bonded O atoms, the increase in E_r is about equal to that for the bonding of two N atoms, and the increase in δH for Ni^{2+} to that for four N atoms. The effect of these ring systems on stabilization energies can thus be summarized:

TABLE XX

Average Values of E_r and δH for Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} Complexes of β-Diketones and Similar Ligands

Ligand	No. of ligands	Max. no. of examples	E_r (Mn–Zn)	δH, kcal/mole			
				Fe	Co	Ni	Cu
Salicylaldehyde	1	1	48	17	25	35	30
β-Diketones	1	5	47.6 ± 0.5	18.4 ± 0.7	25.6 ± 0.5	35.8 ± 0.6	30.7 ± 0.4
Tetracyclines	1	3	47.3 ± 0.4	18.3 ± 0.9	25	35.5 ± 0.5	29.3 ± 0.4
2-Nitroso-1-naphthol	1	1	49			38	
Salicylaldehyde	2	1	49	17	25	36	33
β-Diketones	2	6	48 ± 2	20.7 ± 1.1	27 ± 1	37.3 ± 0.7	34.2 ± 1.2
2-Nitroso-1-naphthol	2	1	51			41	



Hydroxynitroso β-Diketone Carboxylate ($x = 0$ and 1)

As more data become available, it is likely that similar correlations will be found for ligands with other bonding atoms and other chelate ring systems.

In Section IV-D-3 we shall see how δH and E_r are affected when the oxygen and nitrogen are part of more complicated ligands, especially those containing conjugated aromatic rings. But before proceeding we will examine the few E_r and δH values, listed in Table XXI, which can be obtained from experimental determinations of ΔH_c. Comparison with the previous 29 values shows satisfactory agreement in some cases but not in others: eleven of the values are within 1 kcal./

TABLE XXI
Data for Various Complexes of Mn^{2+} . . . Zn^{2+} Based on Experimental Values of ΔH_c

Ligand	No. of ligands	E_r (Mn–Zn)	δH, kcal./mole Fe	Co	Ni	Cu	Ref.[a]
Acetylacetone	1	48		26	36	26	I *120*, 4
	2	48		27	40	29	
8-Hydroxy-2-methylquinoline[b]	2	51		27	35	33	I *350*, 1, 2, 3
8-Hydroxy-4-methylquinoline[b]	2	55		30	42		I *351*, 1
2,2′-Diaminodiethylamine	1	51	20	28	38	38	I *86*, 2
N,N′-Di-(2-aminoethyl)-ethylenediamine	1	48	21	27	42	43	I *189*, 3
Ethylenediamine-*N,N,N′,N′*-tetraacetic acid	1	46		24	36	29	I *362*, 3; c

[a] For I *120*, 4, etc., see ref. 30.

[b] Measurements made on dioxane–water solutions.

[c] R. G. Charles, *J. Amer. Chem. Soc.*, *76*, 5854 (1954).

mole; six are within 2 kcal./mole; six are within 3 kcal./mole; and five deviate by more than 4 kcal./mole. It may be significant that four of the seven E_r values deviate by 3 or more kcal./mole, and, should either of the Mn^{2+} or Zn^{2+} values from which E_r is obtained be in error, this would be further reflected in the values of δH. Undoubtedly, the experimental values of ΔH_c are known with less certainty than are stability constants. Unfortunately, only two of these ligands are among the 22 used to establish the correlations among E_r, δH, and the number of bonded N atoms, so a searching comparison cannot be made. It seems probable, though, that δH values calculated by the present procedure would be subject to systematic error and that the same linear relationships would hold for values obtained from experimental values of ΔH_c.

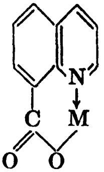
3. A Comparison of Stabilization Energies for Various Ligands

Having established the main trends in δH and E_r for coordination with oxygen- and aliphatic nitrogen-bonding groups, we are now in a position to compare the values for other ligands which have more diverse chemical structures.

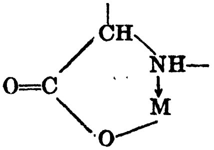
a. Inorganic Ligands. In all cases the E_r and δH values for Cl^-, SO_4^{2-}, and $S_2O_3^{2-}$ are less than, or equal to, the values for H_2O.

b. Glycylglycine. In all cases the E_r and δH values are a little less than those for the bonding of one N atom. This may be a result of coordination via the terminal NH_2 group, the corresponding group in the α-position with respect to the free carboxyl group being converted into a peptide link, the nitrogen of which forms weaker complexes.

c. Quinoline-8-carboxylic Acid. All the values are low with the exception of that for Cu^{2+}. It may be noted that coordination with this ligand gives a six-membered ring (VI) in contrast to the five-membered ring (VII) formed by the other α-amino- and α-iminodicarboxylic acids.

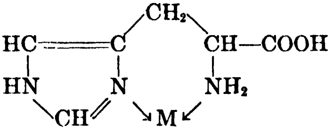


(VI)



(VII)

d. Histidine. With the exception of those for Cu^{2+}, the values for combination with one and two histidines are approximately equal to those for coordination with two and four N atoms, respectively, an indication of bonding via the α-NH_2 group and the glyoxaline N atom of the ring (VIII) instead of the carboxyl group.



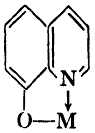
(VIII)

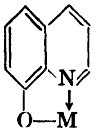
e. Cysteine and 2-Mercaptoethyliminodiacetic Acid. Disregarding the anomalous low value for Ni^{2+} with the latter ligand, E_r and the other δH values, which are consistently higher, suggest that bonding via —S^- occurs: from Figure 10 it would appear that one bonded S atom has an effect equivalent to two bonded N atoms. The observation that all the values for the two thioethers, i.e., 2-methylthioethyliminodiacetic acid in Table XV and 2,2′-bis[di(carboxymethyl)amino]-diethyl sulfide in Table XVI, are in accord with the bonding of only oxygen and nitrogen, is also good evidence that a mercapto group is necessary for bonded sulfur to show the extra stabilization effect.

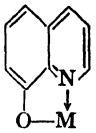
f. Ethylenediamine-N,N-diacetic and Ethylenediamine-N,N′-dipropionic Acids. The high values throughout are in keeping with the bonding of two N atoms per ligand instead of one, as is the case with the other amino- and iminocarboxylic acids in Table XV.

g. Iminotri- and Iminotetracarboxylic Acids. Except for nitrilotriacetic acid these ligands bond two N atoms per molecule. In all but one case the values of δH for Cu^{2+} are very low. The values of E_r are a little low, whereas the values of δH for Co^{2+} and Ni^{2+} agree well with those predicted from Figure 10. With these polydentate ligands, steric effects, which are not present in the coordination of the simpler amino and imino acids, may be important.

h. Hydroxyquinolines, 4-Hydroxypteridine, and Pteroylglutamic Acid. The three substituted 8-hydroxyquinolines in Table XVII and these other two ligands coordinate to give an identical five-membered chelate ring (IX) which is similar to VII in the disposition of the atoms, but differs in that the carbon and nitrogen form part of heterocyclic aromatic systems. Resonating structures for complexes with the parent compound can be written as IXa, b, c. For the combina-

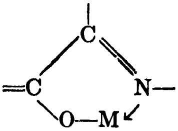

(IXa)


(IXb)


(IXc)

tion of both one and two ligand groups, there is close agreement in the majority of cases with the corresponding E_r and δH values for the bonding of one and two aliphatic N atoms (see Fig. 10). Unless there is a fortuitous interplay of effects, two conclusions can be drawn: (*1*) that a tertiary N atom in an aromatic system on forming a five-membered ring is equivalent to an aliphatic amino or imino nitrogen atom and (*2*) that coordination by a phenolate oxygen atom influences the ligand field to the same extent as the oxygen of a carboxylate ion or a water molecule. It can be seen that chelate rings of this type do not give rise to the same kind of resonating structures as those characteristic of the six-membered rings formed by salicylaldehyde (III), the β-diketones (IV), and 2-nitroso-1-naphthol (V). This may be an important factor determining the magnitude of E_r and δH, and will be brought up again later in connection with the azo dyes, and in the final discussion (Sections IV-D-3(m) and IV-D-4).

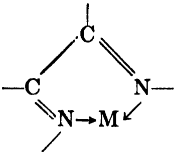
i. Riboflavin. In this case the chelate ring (X), although made up of the same atoms as IX, contains an isolated double bond by virtue of the quinonemonoimine type of structure in the parent com-


(X)

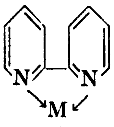
pound. Compared to IX the decrease in the C–N bond length would result in a slight contraction of the ring, and it may be noted that the δH values for Co^{2+} and Ni^{2+} are significantly lower than those for either IX or VII.

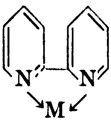
j. Dimethylglyoxime O-Monomethyl Ether. The values of E_r and δH are somewhat conflicting. The addition of one and two ligand groups provides two and four bonding N atoms, respectively; but, while the values of δH for Co^{2+} are in accord, E_r and δH for Ni^{2+} and Cu^{2+} are extremely low. The formation of planar rather than octahedral complexes with this type of ligand is well established, and this would explain the discrepancy, because with planar complexes the *d* orbital splitting is different (see Section I).

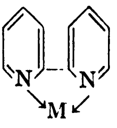
Another feature of the bonding of this ligand is the formation of a five-membered ring containing two double bonds (XI), so, in comparison with the other five-membered ring systems, it will be subject to the greatest contraction.


(XI)

k. 2,2'-Dipyridyl and 1,10-Phenanthroline. The values of E_r and δH for the tris complexes of Co^{2+} and Ni^{2+} are in reasonable agreement with the values predicted for the bonding of six N atoms (see Fig. 10). This bears out the inference based on the 8-hydroxyquinoline data that a tertiary N atom in an aromatic ring is equivalent to an aliphatic amino or imino N atom in many cases. It is not surprising to find the very low values of δH for the corresponding complex of Cu^{2+}. Six-fold coordination about this ion has been found to exhibit tetragonal symmetry, with four groups equidistant in a plane and the fifth and sixth groups completing the octahedron at a greater interatomic distance (10). Preferred bonding of this kind cannot be readily attained by the combination of three bidentate ligands, such as 2,2'-dipyridyl and 1,10-phenanthroline, in which the aromatic conjugation favors a rigid five-membered chelate ring. In the case of 2,2'-dipyridyl, for example. the resonance structures are XIIa, b, c.

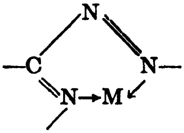

(XIIa)


(XIIb; two forms)


(XIIc)

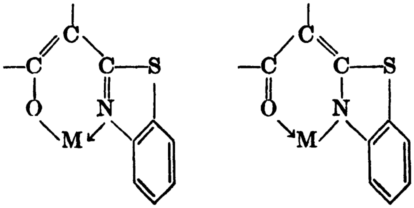
On the other hand, the values of δH for the tris complexes of Fe^{2+}, 30 and 33 kcal./mole, are exceptionally high. None of the other values in Tables XIII–XVIII exceed 22 kcal./mole, and for the bonding of aliphatic nitrogen 20 kcal./mole is the greatest. Unlike all the other complexes, however, magnetic susceptibility measurements have shown these to be of the low spin type, and ligand field theory would predict larger stabilization energies in just these cases. A similar "spin quenching" phenomenon was mentioned as the probable cause of the large δH values of FeSe and FeTe in Section II-C.

l. 2-p-Dimethylaminophenylazopyridine. The five-membered chelate ring (XIII) formed by this ligand does not participate in the single-double bond resonating structures of a conjugated aromatic system. The values of E_r and δH, except that for Cu^{2+}, are in good agreement with those expected for the bonding of two N atoms.

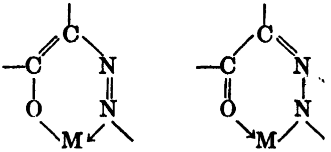


(XIII)

m. 2-(o-Hydroxyphenyl)benzothiazole and the Hydroxyazo Dyes (Table XVII). These ligands are bi- and tridentate, providing one bonding N atom and one and two bonding O atoms, respectively, per ligand group. With the thiazole, the value of E_r agrees with that for one bonded N atom, but the values of δH are appreciably higher, in the case of Cu^{2+} as high as that for the bonding of four atoms (see Fig. 10). With the azo dyes, the values of E_r and δH for Ni^{2+} and Cu^{2+} are approximately equal to the values for the bonding of two N atoms, and the values of δH for Co^{2+} are even greater. The increased values in these cases may be connected with the fact that the chelate rings contain six atoms and two double bonds, like those for sali-



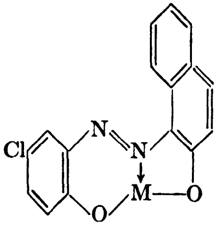
(XIV)



(XV)

cylaldehyde (III), the β-diketones (IV), and 2-nitroso-1-naphthol (V), and similar resonating structures can be written for thiazole (XIV) and the azo dyes (XV). Bonding via the S atom instead of the N atom in the thiazole ring is unlikely in view of the lack of evidence for extra stabilization through coordination with the S atoms in thioethers(see Section IV-D-3(e)).

On this basis we would not necessarily expect the values for the tridentate azo dyes to be greater than those for the bidentate thiazole, because the second chelate ring that is formed (XVI) contains only five atoms, and can only contribute additional resonating structures similar to those for hydroxyquinolines (XIa, b) where no increase in δH values was found.



Complex with 1-(5-chloro-2-hydroxyphenylazo)-2-naphthol
(XVI)

4. Summary and Conclusions

The present calculations have borne out the conclusion, reached in an earlier paper, that E_r and the stabilization energies for many complexes are determined solely by the atoms directly bonded to the metal ion, the structure of the rest of the ligand group having far less influence (32). The same conclusion has been drawn from the analysis of optical spectra, which is particularly gratifying in view of the interrelationship predicted by ligand field theory (1,2). With thermodynamic data for many more complexes now available, especially for a large variety of chelate ring systems, it has been possible to examine the role of structural factors in greater detail. Yet it should be emphasized that until experimental determinations of the heat of complex formation in aqueous solution have been made, the conclusions summarized below must be regarded as tentative and taken to illustrate the kind of correlation that can be looked for.

With a great variety of ligands containing bonding N atoms, which range from aliphatic polydentate amines, amino acids, imino polycarboxylic acids, heterocyclic amines, and hydroxyamines with tertiary N atoms in aromatic ring systems, to azo compounds, the values of E_r and δH for Co^{2+}, Ni^{2+}, and Cu^{2+} complexes containing up to four N atoms show an approximately linear increase with the number of bonded N atoms. E_r and δH for Cu^{2+} decrease upon further coordination, but the values for Co^{2+} and Ni^{2+} still follow the linear dependence (Fig. 10). The values of δH for Fe^{2+} show a much smaller increase, and δH for corresponding complexes invariably follows the order:

$$Ni^{2+} > Cu^{2+} > Co^{2+} \gg Fe^{2+}$$

That such simple relationships hold for all these ligands enables the following conclusions to be drawn regarding the influence of various structural factors upon the magnitude of stabilization energies.

1. The contribution of an O atom is the same (to within 1 kcal./mole), no matter whether it is in a water molecule, a carboxylate ion, or a phenolate ion; hence charge cancellation plays an insignificant part in determining stabilization energies. This is demonstrated very clearly by the same values obtained for coordination with one ethylenediamine, with two aminomonocarboxylic acids, and with two iminodicarboxylic acids, ligands which leave the charge on the metal ion unchanged, diminish it by two units, and diminish it by four units, respectively. Charge cancellation is also an unimportant factor in some crystalline compounds, since, as we saw in Section II, very similar δH values are obtained for the M^{2+} chlorides and oxides, which have singly charged and doubly charged anions at the lattice points, respectively. This conclusion emphasizes the role of the more general ligand field theory, because, in terms of a simple electrostatic model, charge effects would be expected to be of paramount importance.

2. The data which are available for two ligands containing —SH groups indicate that one bonded S atom exerts an influence in the ligand field equivalent to two bonded N atoms. There is no evidence however, for stabilization arising from the bonding of sulfur in thioethers.

3. All the organic ligands discussed are bi- or polydentate, and the data can most conveniently be summarized according to whether five- or six-membered chelate rings are formed (see Table XXII). The diversity of structure is well brought out by the fact that eight

TABLE XXII

Order of Decreasing Stabilization Energies for Five- and Six-membered Chelate Rings[a]

Five-membered rings								
	XII =	XIII =	XVI >	IX =	VII >	X =	XI >	I
Bonding atoms	$2\ N_{res.}$	$2\ N_{res.}$	2 N	N, $O_{res.}$	N, O	N, O	2 N	2 O
Six-membered rings								
	XIV ≥	XV >	VIII >	VI >	V >	IV =	III >	II
Bonding atoms	$2\ N_{res.}$	$2\ N_{res.}$	2 N	N, O	$2\ O_{res.}$	$2\ O_{res.}$	$2\ O_{res.}$	2 O

[a] Key to Ligands: I, oxalate; II, malonate; III, salicylaldehyde; IV, β-diketones; V, 2-nitroso-1-naphthol; VI, quinoline-8-carboxylic acid; VII, amino- and iminocarboxylic acids; VIII, histidine; IX, 8-hydroxyquinolines; X, riboflavin, XI, dimethylglyoxine *O*-monomethyl ether; XII, 2,2′-dipyridyl and 1,10-phenanthroline; XIII, 2-*p*-dimethylaminophenylazopyridine; XIV, 2-*o*-hydroxyphenylbenzothiazole; XV, hydroxyazo dyes (see Table XVII); XVI, ethylene diamine.

The subscript "res." indicates that single-double bond resonating structures, which include the bonding atoms, can be written for these ring systems.

different ring systems of each type are exemplified. With the single exception of the glyoxime (XI), the stabilization energies for the five-membered chelate rings are in good agreement with the number of bonded N atoms, even though single-double bond resonance structures can be written for some but not for others. With the six-membered ring systems, however, only those conform for which single-double bond resonance structures cannot be written; in the other cases consistently higher stabilization energies are obtained. The most extensive data are for oxygen-bonding ligands (III-V), and the stabilization energies are found to be a linear function of the number of bonded O atoms (Fig. 11). The contribution made by this additional stabilization is relatively small compared to nitrogen bonding, four bonded O atoms ≡ one bonded N atom. A significant difference between the resonance structures for the five- and six-membered rings is that only with the latter do the individual structures contain the same number of double and single bonds. Furthermore, two double bonds are already present (III–V, XIV, XV), so that if the metal ion can rise from a π-bond to one of the ligands, three double bonds result, and the ring becomes pseudoaromatic in character. This structural feature, restricted to these particular six-membered ring systems, offers a plausible explanation for the enhanced stabilization energies.

4. Finally, with a knowledge of the stabilization energies to be expected from the bonding of typical atoms, the values for complicated ligands can be used to suggest which of the groups are bonded to the metal.

E. A COMPARISON OF THE THERMODYNAMIC STABILIZATION ENERGIES WITH THOSE CALCULATED FROM OPTICAL DATA

As in the case of the hydrated ions, the splitting parameter, *Dq* or Δ, where $\Delta = 10Dq$, can be obtained from optical data, and the contribution to the stabilization energy, arising directly from the splitting of the *d* orbitals, can be calculated by multiplying *Dq* by the appropriate factors. The ligand field strength varies over the range of coordination compounds discussed, but for the complexes of Fe^{2+}, Ni^{2+}, and Cu^{2+} the same factors, 4, 12, and 6, respectively, hold for both weak and strong fields. However, with Co^{2+}, whereas the weak field factor of 6 is applicable to the hydrated ion, it is not certain whether this factor, or the strong field factor of 8, or one of intermediate magnitude, should be employed for the two complexes discussed below; various values will therefore be considered. The optical data tabulated by Jørgensen (10) have been used in the calculations, supplemented by a few observations of our own on Cu^{2+} complexes (see the caption of Fig. 13).

There are very few Fe^{2+} and Co^{2+} complexes for which a comparison can be made at present. For Fe^{2+} the thermodynamic and optical δH values for both the aquo-ion and the ethylenediaminetetraacetate complex are 17 and 11 kcal./mole, respectively, and thus differ by an equal amount. For Co^{2+}, the thermodynamic and optical δH values are listed Table XXIII for the aquo-ion and the ethylenediaminetetraacetate and trisethylenediamine complexes. On the basis of the strong field factor, the values for the trisethylenediamine complex and those for the aquo-ion also differ by an equal amount, while for the ethylenediaminetetraacetate complex the difference is larger than that for the aquo-ion with the weak field factor and smaller with the strong field factor. An intermediate value of 7, however, gives the same difference. Factors of 7 and 8 for the ethylenediaminetetraacetate and trisethylenediamine complexes are not unreasonable,

TABLE XXIII

A Comparison of the Thermodynamic Stabilization Energies for Co^{2+} Complexes with Values Calculated from Optical Data (—), Using both Weak and Strong Field Factors

Ligand	Thermodynamic δH	Optical δH	
		6Dq	8Dq
Water (i.e., the aquo-ion)	24	17	
Ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid	27	17	23
(Ethylenediamine)$_3$	32	19	25

since two and six N atoms, respectively, are coordinated, which would lead to a progressive increase in ligand field strength.

To compare values for Ni^{2+} and Cu^{2+} complexes, since many more

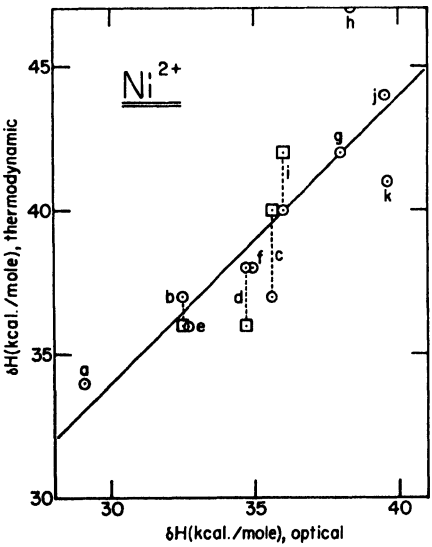


Fig. 12. The stabilization energies for Ni^{2+} obtained from thermodynamic data plotted against the values obtained from optical data for various ligands: (*a*) water, (*b*)(acetylacetone)$_1$, (*c*) (acetylacetone)$_2$, (*d*) (ethylenediaminetetraacetate)$_1$, (*e*) (nitrilotriacetate)$_1$, (*f*) (ethylenediamine)$_1$, (*g*) (ethylenediamine)$_2$, (*h*) (ethylenediamine)$_3$, (*i*) (2,2′,2″-triaminotriethylamine)$_1$, (*j*) (2,2′-dipyridyl)$_3$, (*k*) (1,10-phenanthroline)$_3$. O values from relative ΔH_c data and optical data in ref. 10; □ values from experimental ΔH_c data and optical data in ref. 10.

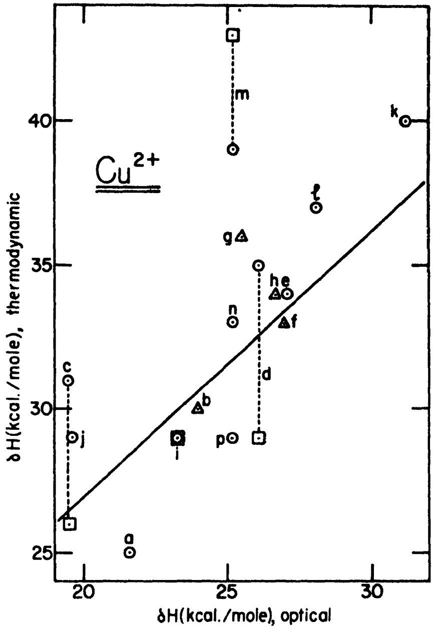


Fig. 13. The stabilization energies for Cu^{2+} obtained from thermodynamic data, plotted against the values obtained from optical data for various ligands: (*a*) water, (*b*) (oxalate)$_2$, (*c*) (acetylacetone)$_1$, (*d*) (acetylacetone)$_2$, (*e*) (glycine)$_2$, (*f*) (valine)$_2$, (*g*) (tryptophane)$_2$, (*h*) (histidine)$_2$, (*i*) (ethylenediaminetetraacetate)$_1$, (*j*) (nitrilotriacetate)$_1$, (*k*) (ethylenediamine), (*l*) (ethylenediamine)$_3$, (*m*) (2,2′,2″-triaminotriethylamine)$_1$, (*n*) (2,2′-dipyridyl)$_3$, (*p*) (1,10 phenanthroline)$_3$. ○ values from relative ΔH_c data and optical data in ref. 10; □ values from experimental ΔH_c data and optical data in ref. 10; △ values from relative ΔH_c data and authors' optical data.

are available, the two stabilization energies are plotted against each other in Figures 12 and 13. In the case of Ni^{2+} the points lie rather well about a 45° line, but are displaced so that the thermodynamic values are consistently greater by about 4 kcal./mole. The point for the aquo-ion is in good agreement. Thus the difference between the values for the complexes is again approximately equal to the difference between the values for the aquo-ion. In the case of Cu^{2+}, the points show a greater scatter. If a 45° line is drawn through the central cluster of points, the point for the aquo-ion lies well away. Thus, while the difference between the values for the aquo-ion is 3

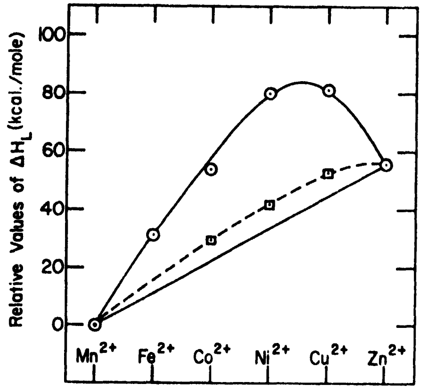


Fig. 14. The values of ΔH_L for the trisethylenediamine complexes of Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} relative to the value for Mn^{2+} plotted against atomic number, together with the interpolated ΔH_L curve (– – –) obtained by subtracting the optical stabilization energies from the ΔH_L values for the Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} complexes.

kcal./mole, the difference for the complexes, based on the 45° line, would be about 7 kcal./mole. In the few instances where thermodynamic δH values can be calculated from experimental ΔH_c data (Table XXI), these have also been plotted in the figures, but only a haphazard shifting of the points results.

Since the thermodynamic stabilization energies for the aquo-ions are greater than those calculated from optical data, ΔH_H values plotted against atomic number, after subtracting the contribution from *d* orbital splitting on the basis of the optical data, follow a curve which is slightly concave with respect to the atomic number axis (Fig. 7). The thermodynamic stabilization energies for the coordination complexes discussed above also exceed the values calculated from optical data. Hence the interpolated values of ΔH_L will also follow a concave curve, as illustrated in Figure 14 for the trisethylenediamine complexes. Moreover, since the differences between the thermodynamic and optical stabilization energies for the Fe^{2+}, Co^{2+}, and Ni^{2+} complexes are approximately equal to the differences between the values for the aquo-ions, in the region Mn^{2+}–Ni^{2+} the curve for the interpolated values of ΔH_L will approximate very closely the curve for the interpolated values of ΔH_H. The data for the Cu^{2+} complexes, on the other hand, indicate that, in general, the interpolated ΔH_L value for Cu^{2+} will deviate from the interpolated ΔH_L curve, lying above it. This follows from Figure 13, where it can be seen that a line with a slope greater than 45° passing through the point for the aquo-ion would give a better fit, which implies that some extra stabilization is present in these complexes over and above that estimated from the optical stabilization energy. Similar anomalous behavior has also been noted in the discussion of lattice energies of Cu^{2+} compounds in Section III. One contributing factor is undoubtedly the preferred tetragonal symmetry about the Cu^{2+} ion, since any calculation of a thermodynamic stabilization energy for Cu^{2+} derivatives that involves data for the other ions where octahedral symmetry predominates is clearly a rather gross approximation.

These conclusions regarding the variation of the interpolated values of ΔH_L with atomic number have a bearing on a question raised in Section IV-B. It was shown there that the quantities ΔH_H and ΔH_L do not relate to single chemical reactions, but are made up of several terms:

$$\Delta H_H = \Delta H_{\mathrm{hyd}} + \Delta I_{\mathrm{soln,\ hydrated\ ion}} + 6\lambda_{\mathrm{H_2O}} \tag{26}$$

and for the complex ion containing six ligand groups:

$$\Delta H_L = \Delta H_{\mathrm{com}} + \Delta H_{\mathrm{soln,\ complex\ ion}} + 6(\mathrm{S_{lig}} + \lambda_{\mathrm{lig}}) \tag{27}$$

where ΔH_{hyd} and ΔH_{com}, the fundamental heats of formation of the hydrated ion and the complex ion in the gas phase, contain the ligand field stabilization energies. Hence, for the values of ΔH_H and ΔH_L to reflect accurately these stabilization energies, the heat of solution terms should be the same throughout the series $Mn^{2+} \ldots Zn^{2+}$ ($\lambda_{\mathrm{H_2O}}$, S_{lig}, and λ_{lig} being common).

Heats of solution can be estimated using the Born charging equation:

$$\Delta F_{\mathrm{B.C.}} = (-Z^2e^2/2R)\,(1 - 1/D) \tag{32}$$

which gives the free energy of formation of a spherical cavity of radius R, bearing a charge Ze, in a continuous medium with dielectric constant D. Differentiation of eq. 32 with respect to temperature gives the entropy charge, and from the equation $\Delta H = \Delta F + T\Delta S$, it follows that

$$\Delta H_{\mathrm{B.C}} = (-\,Z^2e^2/2R)\,[(1 - 1/D) + (T/D^2)(\partial D/\partial T)_p] \tag{33}$$

If hydrated ions and complex ions are regarded as charged spheres, and the solution process as the introduction of these spheres into a continuous water dielectric, then insertion of numerical values in eq. 33 gives for the heat of solution,

$$\Delta H_{\text{soln}} = -669/R \text{ (kcal./mole)} \tag{34}$$

where R is the radius in Angstrom units.

The radius of a hydrated ion can be taken as the sum of the ionic radius and the diameter of the water molecule (2.76 A.); and values for the heats of solution, calculated from eq. 34 using Goldschmidt's ionic radii (0.91, 0.83, 0.82, 0.78, 0.72, and 0.83 A. for the ions Mn^{2+} ... Zn^{2+}), are plotted against atomic number in Figure 15. A slightly humped curve is obtained, with the values for Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} lying 3, 3, 5, and 7 kcal./mole, respectively, above the line joining the values for Mn^{2+} and Zn^{2+}. These increments are so much like the corresponding increments in the plot of the interpolated values of ΔH_H, i.e., 6, 4, 5, and 3 kcal./mole, as to suggest that the slightly different heats of solution of the hydrated ions, arising from the small alteration in ionic radius, account for the variation.

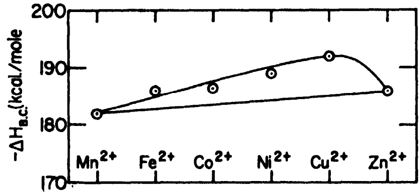


Fig. 15. Heats of solution for the aquo-ions Mn^{2+} . . Zn^{2+}, obtained by calculation from the Born charging equation, plotted against atomic number.

However, the complex ions have larger radii and correspondingly smaller heats of solution. For trisethylenediamine complexes, some of the smallest, the radii estimated from Courtauld atomic models will be about 4.4 A., and as a consequence the increments in ΔH_{soln}. are decreased to about 2, 2, 3, and 4.5 kcal./mole for the Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} complexes, respectively. With the larger complex ions these increments will be smaller still. Yet, as shown above, there is substantial evidence in the case of Ni^{2+} complexes, and a good indication from the fewer values for Fe^{2+} and Co^{2+} complexes, that the curves for interpolated ΔH_L values follow the curve for the interpolated ΔH_H values very closely. Hence, it seems unlikely that a variation in heats of solution can be the correct explanation. If this is so, then the thermodynamic stabilization energies calculated from eq. 30 contain no contribution from a heat of solution term. A further consideration is that the use of the Born charging equation to calculate solution energies is open to criticism on the grounds that it is based on a classical electrostatic model and makes use of a continuous dielectric, whereas the solution process is one of interaction at the molecular level. The experimental evidence which suggests that heats of solution do not play a significance role is nevertheless still valid.

The values of E_r, the difference between ΔH_L for the Zn^{2+} and Mn^{2+} complexes with the various ligands, call for comment at this point. First, it can be seen from Table V that E_r ranges over very similar values with the common crystalline compounds, e.g., halides, oxides, etc. In only three of the ten cases—i.e., the sulfides, selenides, and tellurides, for which E_r is 62, 69, and 71 kcal./mole, respectively—do the values exceed the greatest value of 60 kcal./mole found for 1,10-phenanthroline among the coordination complexes. Second, although *d* orbital splitting cannot contribute a purely electronic stabilization energy term in the case of complexes containing the d^5 or d^{10} ions, large stabilization energies for Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} are often accompanied by large values of E_r. This is especially true for the series of aliphatic polydentate amines, aminomonocarboxylic acids, and iminodicarboxylic acids (Tables XIV,

TABLE XXIV

The Relation between E_r and δH for Co^{2+}, Ni^{2+}, and Cu^{2+} for the Bonding of Aliphatic Nitrogen Atoms

No. of bonded N atoms	$E_r/\delta H_{Co^{2+}}$	$E_r/\delta H_{Ni^{2+}}$	$E_r/\delta H_{Cu^{2+}}$
0	2.0	1.4	1.9
1	1.9	1.4	1.7
2	1.9	1.4	1.6
3	2.0	1.4	1.5
4	2.0	1.4	1.5
5	—	1.4	1.5
6	1.8	1.3	1.5

XV, XVIII, and XIX). Not only is E_r a linear function of the number of bonded N atoms for complexes with up to four bonded N atoms (see Fig. 10) but, as shown in Table XXIV, the quotient $E_r/\delta H$, with δH for Co^{2+}, Ni^{2+}, and Cu^{2+}, remains remarkably constant over the whole range from one to six bonded N atoms. This numerical agreement is probably fortuitous, because in the detailed discussion of values for other ligands in Section IV-D-3 there are several instances of low E_r values along with high values of δH. Yet the fact that there is a correlation in quite a number of cases suggests that certain ligand field systems possess a common property that can lead both to large splitting parameters, and hence large stabilization energies, and to enhanced metal ion–ligand interaction energies independent of the number of *d* electrons.

F. ELECTRON AFFINITIES AND STABILITY CONSTANTS OF THE TRANSITION METAL IONS,

Before the application of ligand field theory to the stability of coordination complexes, it was suggested that the variation of log (stability constant) in the series $Mn^{2+} \ldots Zn^{2+}$, rising to a sharp peak at Cu^{2+} (curve *a*, Fig. 16), is due to the variation in electron affinity of

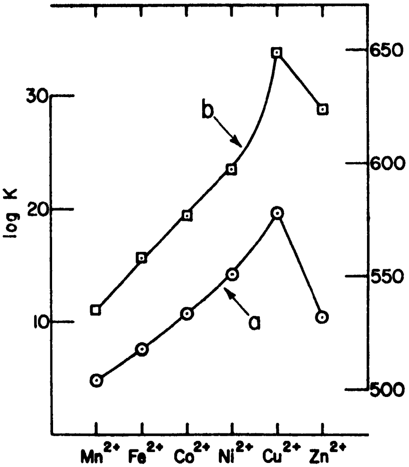


Fig. 16. The variation of (*a*) log (stability constant) for the formation of the trisethylenediamine complexes and (*b*) $E_{M^{2+}}$, the electron affinity of the M^{2+} ions, with atomic number, in the series $Mn^{2+} \ldots Zn^{2+}$.

the metal ion (35,36). If this quantity, given by the sum of the first and second ionization potentials of the metal, is plotted against atomic number, a curve having a somewhat similar shape is obtained (curve *b*, Fig. 16). The plot of log (stability constant) is equivalent to a plot of ΔF, and since ΔS for complex formation is approximately constant throughout the series, the relationship implied is one between ΔH_c and electron affinity.

However, ΔH_c is the difference between the two more fundamental thermodynamic quantities, ΔH_L and ΔH_H (eq. 25), and these quantities show an entirely different variation with atomic number. Both ΔH_H and ΔH_L increase greatly from Mn^{2+} to Ni^{2+} and pass through a flat maximum between Ni^{2+} and Cu^{2+} (Figs. 9 and 14). Furthermore, we have seen in the preceding discussion how ligand field stabilization accounts to a very large extent for the greater ΔH_H and ΔH_L values for Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}. After subtracting the stabilization energies calculated from optical data, the interpolated values of ΔH_H and ΔH_L fall on a smooth curve rising from Mn^{2+} through Fe^{2+}, Co^{2+}, and Ni^{2+} to Zn^{2+}, with the values for Cu^{2+} complexes tending to show deviations attributable to the preferred tetragonal symmetry. The general equation giving ΔH_c for the Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} complexes in terms of ΔH_c for the Mn^{2+} complex, the thermodynamic stabilization energies, and E_r for the aquo-ions and complexes, respectively, can be obtained by combining eqs. 25 and 30:

$$\Delta H_c = \Delta H_{c,\mathrm{Mn}^{2+}} + (\delta H_{\mathrm{L}} - \delta H_{\mathrm{H_2O}}) + [(n - 5)/5](E_{r,L} - E_{r,\mathrm{H_2O}})$$

where $5 < n < 10$. In this equation, the extent to which ΔH_c departs from a linear variation with atomic number is expressed by the term $\delta H_L - \delta H_{\mathrm{H_2O}}$.

In view of these considerations it would appear that the variation of log (stability constant) for the M^{2+} complexes does not have its origin in the electron affinities of the metal ions.

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Mixed Metal Oxides

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I. Introduction

The chemistry of the compounds formed between oxides of the metals deals mainly with the formation, composition, and thermal stability of solid phases. Comparatively little attention has been given to the chemical reactions of the compound once it has been formed. Dissolving these substances in aqueous media, if this can be effected, does not usually lead to the formation of new species, and little has been discovered about the nature of their solutions in fluxes or of the molten mixed oxides themselves. We shall therefore be concerned mostly with their structural chemistry.

Just as the chemistry of metal ions in solution may be rationalized by the recognition of the coordination tendencies of cation and ligand, so also with the solid mixed metal oxides the coordination tendency of the metal ion with oxygen becomes an important factor in explain-ing the existence of compounds. With solids of this type, however, the coordination is generally regarded as predominantly due to the tendency of the cations and oxide ions to assume the closest packing arrangement compatible with local charge balance. Since the oxide ions are usually the larger, they are frequently found in a close-packed arrangement forming tetrahedral and octahedral cavities into which the smaller cations may fit. The large cations may take the place of an oxide ion and hence have a twelve-fold coordination with oxide ions which has no counterpart in the solution chemistry of these cations. The oxide ions always form part of the coordination sphere of several metal ions. This feature makes it possible to describe some of the structures as frameworks or layers of the smaller metal ions held together by metal–oxygen–metal bonds, and it is not an easy matter to decide whether such a structure has a real chemical significance or is merely a convenient way of visualizing the atomic arrangement.

The usefulness of this approach to the chemistry of solids has already been demonstrated in the classification of the silicates. The bewildering variety of these compounds which occur in nature presented a baffling problem to the chemist mainly because there was no solution chemistry of these substances. The mineralogical classification on the basis of crystal symmetry, however, provided the foundation for the determination of the structures of these compounds by X-ray analysis. The elucidation of the chemistry of the silicates sprang from the recognition of the importance of the coordination tendencies of tetravalent silicon and the cations with oxygen.

Silicates are excluded from this discussion because silicon is a nonmetal, but the distinction is quite arbitrary. Mixed metal oxides and silicates may have the same structure, as, for example, in $Y_3Fe_2(FeO_4)_3$ and the garnet $Fe_3Al_2(SiO_4)_3$. We also find compounds whose structures are based on similar principles, such as RbW_3O_9 and $K(AlSi_3O_8)$, the former consisting of WO_6 octahedra sharing all corners forming a framework with large cavities for the rubidium ion which compensates for the partially reduced tungsten and the latter having a framework consisting of SiO_4 and AlO_4 tetrahedra sharing all corners and providing large cavities for the potassium ion which gives the necessary charge balance.

How far analogies of this kind may be carried profitably is difficult to say, but the similarities are further emphasized by the problem of nomenclature. No systematic scheme is available which describes the silicates except in terms of a determined structure. The same situation is encountered with mixed metal oxides. $LiFeO_2$, $LiFe_5O_8$, $LaFeO_3$, $Y_3Fe_5O_{12}$ are all called ferrites, but the environment of the Fe^{3+} ion is different in each case. It is found expedient to refer them to structural types, and this scheme will be used in the discussion to follow. The examples given fall into different groups: $LiFeO_2$ (rock salt), $LiFe_5O_8$ (spinel), $LaFeO_3$ (perovskite), and $Y_3Fe_5O_{12}$ (garnet). It would be convenient if, for these structures, names were available which did not refer to a specific substance. This need is reflected in the common practice of describing the compound—say, Mg_2TiO_4—as a spinel, although the name is specific for $MgAl_2O_4$, but it seems obligatory to refer to $LiNiO_2$ as a rock salt type.

Much of the current research in mixed metal oxides stems from the interest of the electronic industries in exploiting the electrical and magnetic properties of crystalline substances. These properties are of great interest to the chemist because they are extremely sensitive to changes in composition and structure, and intensive study of the relationship should lead to a better understanding of the nature of the chemical bonds in crystals. In considering the different structural types of mixed metal oxides, particular attention will be given to the problems of isomorphous substitution, order-disorder phenomena, cationic and anionic vacancies, nonstoichiometry, and structural variations. A complete survey of the literature is beyond the scope of this chapter. Many of the references given will provide substantial bibliographies. The intention is rather to touch on the more important developments which are of special interest to the chemist.

When the two binary oxides have the same structure, the mixed oxide phase may properly be regarded as a solid solution of the oxides, the range of which may be more or less restricted by the relative ionic radii of the cations. On the other hand, there are many mixed metal oxide phases for which this concept is rather confusing. A considerable proportion of the nickel ions in nickel oxide, which has the rock salt structure, may be replaced by zinc ions without changing the structure. Substitution of nickel for zinc ions in the zinc oxide lattice, however, cannot be effected to any appreciable extent. The environment of the zinc ion is quite different in the two phases, and consequently the nickel–zinc oxide phase should not be regarded as a solid solution of the oxides. It will be expedient in many cases to avoid the use of the concept of solid solutions and to think of such phases as being derived from binary oxides by cationic substitution. This will be indicated by such formulas as $Zn_xNi_{1-x}O$, the substituent being placed first in the formula.

II. Mixed Oxides with the Sodium Chloride Structure

The ideal rock salt structure may be described as a cubic close-packed arrangement of anions in which every octahedral cavity is filled with cations. It is a common structure among the oxides of bivalent metals except palladium, platinum, copper, and the post-transition metals. The simplicity of the structure would seem to offer an attractive testing ground for some of the concepts of solid-state chemistry.

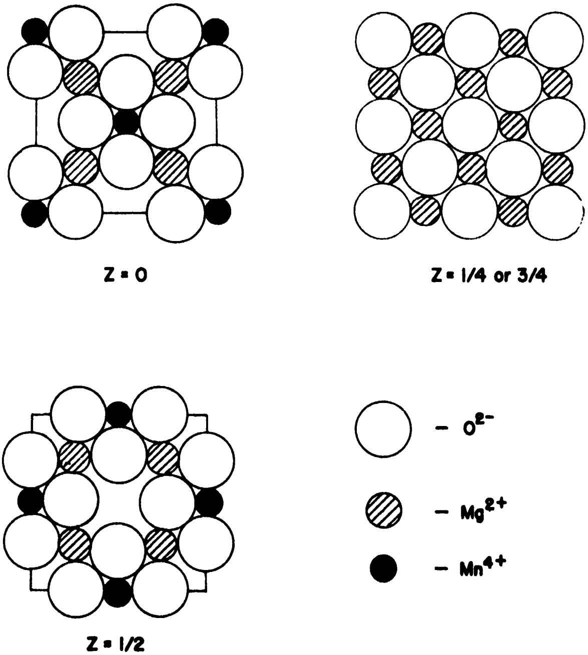


Fig. 1. The structure of Mg_6MnO_8.

The derivation of mixed oxide phases from binary oxides of highly ionic character, such as the oxides of magnesium or the alkaline earths, has not provided phases with very interesting properties except in instances where substituents in low concentrations have given rise to fluorescence. The substitution of manganese for magnesium in magnesium oxide, which is brought about by heating an appropriate mixture of the oxides in air, leads to the formation of a unique phase, Mg_6MnO_8, in which the Mn^{4+} ion replaces two magnesium ions creating a cation vacancy. The vacancies assume an ordered arrangement which gives a unit cell (a = 8.381 A.) about twice the dimensions of the parent magnesium oxide structure (97). The Mn^{4+} ions are also ordered (Fig. 1). A similar phase is obtained with Cu_6PbO_8, although neither PbO nor CuO has the sodium chloride structure.

A. THE CHARACTER OF TRANSITION METAL MONOXIDES

The monoxides of the transition metals which have the rock salt structure differ from those of the alkaline earths in the oxidizable nature of the cations. This feature not only provides a more flexible system for substitution, but also leads to very different properties in the oxides themselves. Some of these differences will be considered before going on to discuss the ternary phases.

Deviation from stoichiometry in transition metal monoxides of this type appears to occur mainly by cation vacancies. The conditions for the existence of ferrous oxide have been carefully examined by Foster and Welch (54) who prepared the monoxide by heating pure iron and ferric oxide in argon at temperatures over 1000°C. followed by rapid quenching. The homogeneity range was established as $Fe_{0.91}O$ to about $Fe_{0.96}O$. Heated at temperatures above 400°, this phase decomposes extensively into Fe_3O_4 and iron. The stoichiometric oxide has not been prepared. In a sense, then, this is a mixed oxide, for the lower limit of the phase may be represented by the formula $Fe^{3+}_{.18}\,Fe^{2+}_{.73}\square_{.09}O$, where $\square$ represents a cation vacancy.

Titanium monoxide exists over the range $Ti_{0.85}O$ to TiO, but Magneli has found that while TiO, prepared at the temperature of the arc, has the sodium chloride structure, annealing at 800°C. leads to a modified structure probably containing ordered ion vacancies (113). A similar structure variant has been obtained by Brauer for niobium monoxide (23) in which both cation and anion vacancies are supposed to exist.

Nickel oxide, at room temperatures, has rhombohedral symmetry but becomes cubic at 275°C. (148). The rhombohedral form is derived from the cubic rock salt structure by a small compression along one of the three-fold axes, as illustrated in Figure 2. At 18°C., the parameters of the unit cell are $a = 2.9518$ A. and $\beta = 60°4.2'$; while in the cubic form at 275°C., $a = 2.9660$ A. and $\beta = 60°$. The transformation to the rhombohedral form on cooling below 275°C. may be due in part to the decreasing effective radius of the nickel ion, but the major factor is probably the spin interaction which leads to an antiferromagnetic arrangement below 250°C. Similar distortions observed in MnO (166,188) and CoO (76) at lower temperatures are also associated with antiferromagnetic ordering.

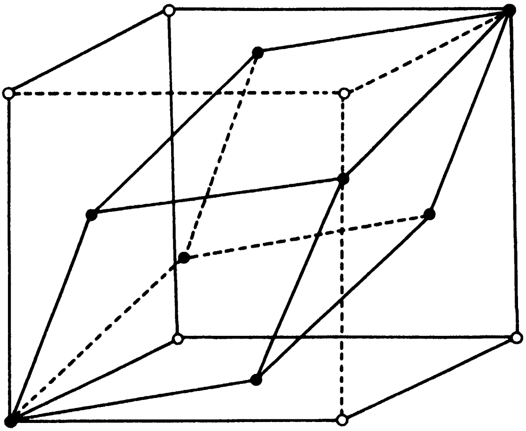
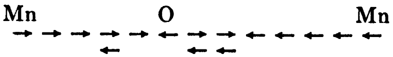


Fig. 2. The relationship of the rhombohedral cell to cubic NaCl.

Interpretations of these physical properties have been made on the basis of exchange interaction between the cations leading to a lower energy state for the system when the spins of the unpaired electrons in neighboring ions are specifically oriented with respect to each other.

Anderson (4) has proposed the existence of a superexchange energy which is the decrease in total energy brought about by the coupling of an electron of the oxygen with one of the $3d$ electrons in the cation causing, in the case of manganese oxide, the antiparallel arrangement.



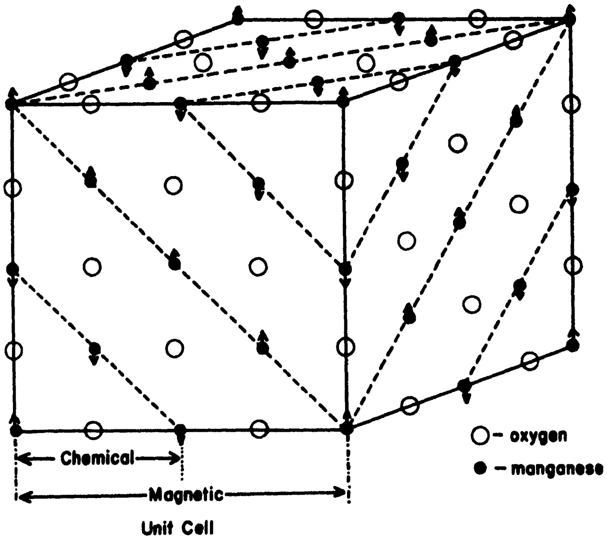


Fig. 3. Spin orientation of Mn^{2+} in MnO showing antiparallel spins of Mn^{2+} ions which are joined by linear Mn–O–Mn bonds.

It is estimated that the decrease in energy would be greatest for a linear M—O—M arrangement and least for a right angle $\begin{array}{ll}\mathrm{M}\text{—} & \mathrm{O}. \\ & | \\ & \mathrm{M}\end{array}$

The spin arrangement predicted on this basis is in agreement with the results of studies by neutron diffraction made below the Curie temperature (166). The unit cell of the magnetic lattice was shown to be twice the crystallographic unit cell. The electron spins are opposed for each manganese connected to another through an oxygen. The spins of all of the manganese ions lying in a plane normal to one of the three-fold axes of the cube are parallel and are opposed to those in the adjacent layers, as illustrated in Figure 3. The connection with the rhombohedral distortion is obvious.

All of these transition metal monoxides are semiconductors, and the *p*-type conductivity of FeO, CoO, and NiO is explained on the basis of cation vacancies (63). The conductivity may be looked upon as an electron transfer from one cation to another (200)

$$M^{2+}\text{—O—}M^{3+} \longrightarrow M^{3+}\text{—O—}M^{2+}$$

which occurs with the greatest facility when the cations involved occupy identical sites. Zener (216) has proposed that such an electronic exchange may favor the adoption of parallel spins by the adjacent cations. This ferromagnetic coupling is called double exchange.

These properties are reflected in the ternary phases obtained by isomorphous substitution in oxides of this kind.

B. MIXED METAL OXIDES OF THE TRANSITION METALS AND ALKALI METALS

Verwey and co-workers (201,202) have shown that the electrical conductivity of nickel oxide is increased spectacularly by the introduction of small amounts of lithium ion as illustrated by the following data:

Specific conductivity	$<10^{-10}$	2×10^{-4}	$\sim 10^{-2}$	$\sim 10^{-1}$	~ 1
x in $Li_xNi_{1-x}O$	0	10^{-4}	10^{-3}	10^{-2}	10^{-1}

The ionic radius of lithium is especially favorable for substitution in the octahedral sites of these oxides. The substitution is accompanied by the oxidation of an equivalent amount of the transition metal to the trivalent state. Thus the formula may be written $Li_xM^{3+}_xM^{2+}_{1-2x}O$. The presumption is that x may vary from 0 to 0.5, and this appears to be true when M = Mn, Fe, Co, Ni. Compounds of this type where $x = 0.5$ have been prepared with M = Ti (214), V, Cr (18), but no attempts seem to have been made to prepare phases with lower values of x with these oxides.

The complete range of composition was first demonstrated by Collongues and Chaudron (36) for the system $Li_xFe_{1-x}O$. The procedure used was to make $LiFeO_2$ by the reaction of Li_2CO_3 with Fe_2O_3 at 700°C. This phase was then heated with an appropriate amount of FeO at 850°C. Samples of $LiFeO_2$ prepared above 700°C. and quenched have a random sodium chloride structure ($a = 4.138$ A.) but apparently undergo a transformation to a tetragonal form ($a = 4.04$ A.; $c = 8.68$ A.) upon annealing in the range 570–670°C. (8,35), which is attributed to an ordering of the metal atoms to an arrangement similar to the ordered zinc blende structure found in $CuFeS_2$. Below 400°C., the structure became tetragonal ($a = 4.07$ A.; $c = 4.28$ A.). The mechanism of the change is apparently not continuous, but resembles a precipitation reaction (37). If the resemblance to the chalcopyrite structure is correct, the Fe^{3+} and Li^+

ions would be in tetrahedral coordination with oxygen. It is interesting to note that both end members of this system, $LiFeO_2$ and FeO, are metastable at room temperatures in the sodium chloride structure.

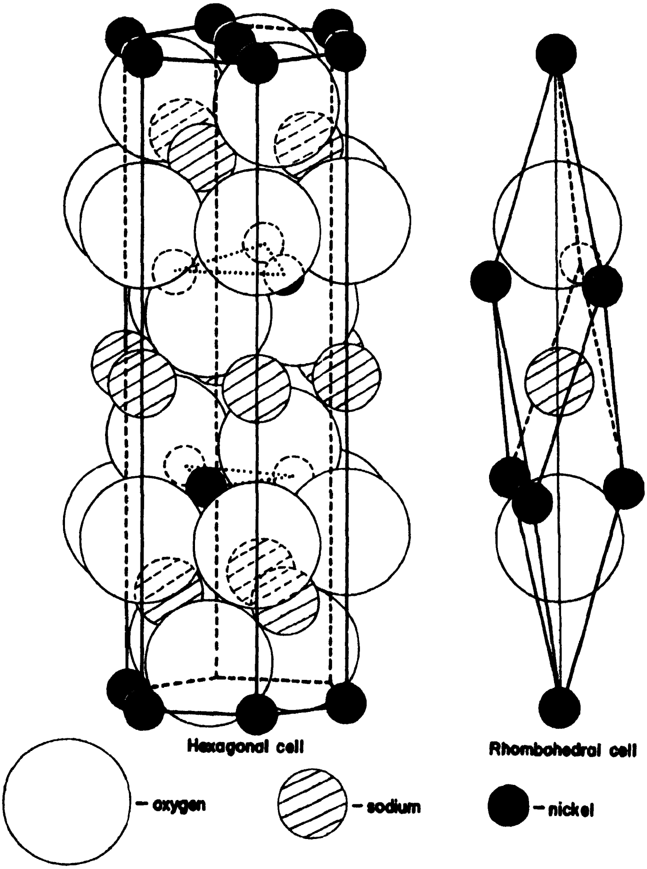


Fig. 4. The layer lattice of $NaNiO_2$ showing the cubic close-packed arrangement of oxide ions joined by alternate layers of Na^+ and Ni^{3+} ions.

The system $Li_xNi^{3+}_xNi^{2+}_{1-2x}O$ illustrates some additional features of this kind of ternary phase. The structures of $LiNiO_2$ and $NaNiO_2$ have been described by Dyer, Bori, and Smith (48) who prepared the compounds by the reaction of fused sodium or lithium hydroxide with elemental nickel in presence of oxygen. The sodium compound was obtained as pure single crystals and was found to be dimorphous, the high temperature form having the same structure as the lithium compound which, however, was not obtained pure. The high temperature form is hexagonal (a = 2.96 A.; c = 15.77 A.), described as having the $CsICl_2$ structure (180) but, from the z parameter given for oxygen, would more nearly correspond to the $NaCrS_2$ structure (19), which is shown in Figure 4. This structure is related to the sodium chloride structure if the (111) planes in which the metal ions lie are alternately occupied by lithium and nickel ions. The environment of each cation is an essentially regular octahedron of oxide ions. (In the $CsICl_2$ structure, the chloride ions are projected almost into the plane of the cations. Should the $LiNiO_2$ structure be strictly analogous, the environment of the metal ions would be quite different).

The low temperature form of $NaNiO_2$ is assigned a monoclinic structure (a = 5.23 A.; b = 2.02 A.; c = 5.59 A.; β = 108.9°), which is formally related to the rhombohedral structure of $NaFeO_2$ (70). The metal atoms are still in octahedral sites, but there is considerable distortion of the octahedron of oxygens around the nickel (4 O at 1.95 A., 2 O at 2.17 A.). It is tempting to attribute such a distortion to the tendency of Ni^{2+} to force a square planar configuration of its ligands (18). Above the transition temperature (~220°C.), the Ni–O distances are all equal at 2.02 A.

Lithium nickel oxide, prepared by interaction of the binary oxides in oxygen at 750° in a magnesium oxide vessel (18), was found to have the composition $Li_{.91}Ni^{3+}_{.90}Ni^{2+}_{.10}O_{1.91}$ by analysis. This substance appeared to be slightly ferromagnetic below 80°K. The asymptotic Curie point, however, was negative. These phenomena are explained on the basis of the formula $(Li_{.95}Ni_{.05})NiO_2$, indicating that a few of the nickel ions are in the lithium layer of the crystal. If pure $LiNiO_2$ could be obtained with a completely ordered structure, each Ni^{3+} ion would be linked linearly through an oxide ion only to lithium ions and would be paramagnetic. The inclusion of a few nickel ions in the lithium layers, on the other hand, would offer the possibility of superexchange among these ions and the six neighboring nickel ions in adjacent layers to which they are joined through Ni—O—Ni linkages. The nickel in the lithium layer would thus create a small ferrimagnetic region in which the central nickel and its six neighbors have opposed spins. From electrostatic consideration, it would seem likely that the nickel ions in the lithium layer would be trivalent rather than divalent, and, hence, superexchange would be more important than double exchange from which one would expect ferromagnetism. This is in agreement with the experimental data.

The fruitless attempts of Dyer (48) and Bongers (18) to obtain stoichiometric $LiNiO_2$ may be attributed to the closeness of the ionic radii of Ni^{3+} (0.68 A.) and Li^+ (0.7 A.), which would be favorable to some randomness in distribution. No difficulty is experienced in the preparation of pure $NaNiO_2$ where the size factor is much more advantageous for the completely ordered structure.

Measurement of the magnetic susceptibility of $NaNiO_2$ as a function of temperature (18) revealed a thermal hysteresis over the range 430–467°K. somewhat below the monoclinic → hexagonal transition temperature. The magnetic moments above and below the transition temperature were 1.76 and 1.9 μ_B, respectively, corresponding to one unpaired electron in each case. An explanation for this is offered on the basis of dsp^2-type bonding, which is specifically oriented in the monoclinic form, but which alternates in the three (100) planes of the octahedron in the hexagonal form. The Ni–O distance of 2.02 A. in the hexagonal form, compared with 2.08 A. for the sum of the ionic radii, is not at variance with the idea. All of the phenomena, including a temperature independent paramagnetism, may be accounted for on the crystal field theory, which does not presuppose electron-pair sharing (18).

In a study of the systems $Li_xM_{1-x}O$ (when M = Mn, Co, Ni Cu) Heikes and Johnston (87) found that the upper limit of values of x for which a homogeneous phase of random sodium chloride structure could be obtained were 0.35 for Mn, 0.2 for Co, 0.15 for Ni, and 0.02 for Cu. Apparently, above these concentrations of lithium the layer structure begins to form as a separate phase. Some evidence has been obtained as a result of diffuse X-ray scattering in the low angle region (52) that short range order exists in $Li_{.2}Co_{.8}O$, each lithium ion being surrounded by more than its statistical amount of transition metal ion. These systems thus differ from the iron system in exhibiting an immiscibility gap within the composition range $0 < x < 0.5$. The manganese system exhibits the smallest immiscibility gap and differs from the others inasmuch as the structure of

$Li_{.5}Mn_{.5}O$ is orthorhombic (a = 2.811 A.; b = 5.763 A.; c = 4.579 A.) (89).

The preparation of $Li_xMn_{1-x}O$ phases was accomplished by heating pressed pellets of intimately mixed lithium peroxide and manganese(II) oxide at 900°C. in an evacuated, sealed container. The reaction

$$^x/_2\ Li_2O_2 + (1 - x)\ MnO \longrightarrow Li_xMn_{1-x}O$$

ensures the stoichiometric quantity of oxygen and thus overcomes the tendency of manganese to oxidize further. This procedure is a convenient general method for the preparation of compounds of this type.

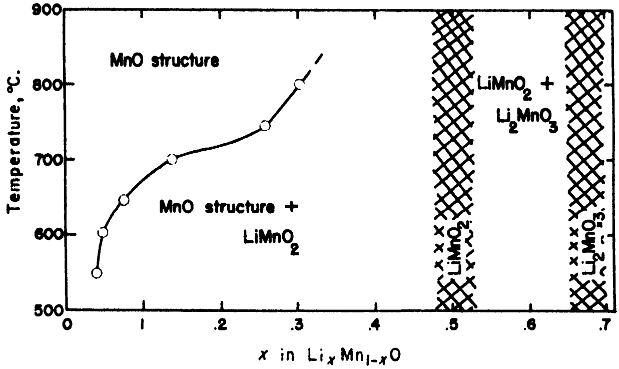


Fig. 5. Phase diagram for $Li_xMn_{1-x}O$.

The phase diagram for the $Li_xMn_{1-x}O$ system appears in Figure 5 which shows that the equilibrium composition of the phase with the sodium chloride structure is x = 0.05 at 550°C. By quenching from 900°C., however, homogeneous samples with this structure could be obtained with values of x up to 0.35.

The assumption that the introduction of lithium ions into the lattice of MnO produces a phase $Li_xMn^{3+}_xMn^{2+}_{1-x}O$ appears to be reasonable. It might be expected that such phases having Mn^{3+} and Mn^{2+} distributed randomly over equivalent crystallographic sites would be electrical conductors and, according to the double exchange theory, would be ferromagnetic, and that there would be an optimum composition. The resistivity was found to decrease with increasing lithium concentration but only up to the surprisingly low value of

$x = 0.1$ (87). The magnetic properties changed from those of a typical antiferromagnetic material to those of a paramagnetic material at about the same lithium concentration. The data appear to suggest that the Mn^{3+} ion in this crystal has zero moment, and that, when the concentration reaches an appreciable value, the crystallographic environment of Mn^{3+} is different from that of the Mn^{2+} ions. The crystal field theory suggests that the environment of Mn^{3+} might be tetrahedral, which would cause the splitting of the *d* levels to provide two low energy levels which could accommodate the four *d* electrons of Mn^{3+}.

The electrical conductivities of most of these solid phases have been measured using compressed, sintered pellets, and, since the numerical values obtained vary with the degree of sintering achieved, direct comparison is not usually possible. It has been found, however, that the activation energies of the process obtained from the log ρ vs. $1/T$ plot are largely independent of the method of sample preparation. In the systems $Li_xM_{1-x}O$, where $M = Mn, Co, Ni, Cu$, it has been found (87) that in all cases the activation energy for conduction decreases rapidly with increasing values of x up to about 0.02 (the limit imposed by the copper system). The activation energy of conduction for $Li_{.02}M_{.98}O$ was found to decrease linearly with increasing atomic number of M from 14 kcal. for the manganese to 2 kcal. for the copper system. It is tempting to correlate this systematic behavior with the increase in number of *d* electrons available.

The antiferromagnetic Curie temperature for the cobalt system (291°K.) lay within the temperature range over which the conductivities were measured. The activation energy of conduction was found to increase abruptly near this temperature, but the difference in the two activation energies decreased linearly with increasing values of x and became zero at $x = 0.2$.

The mathematical interpretation of their data leads Heikes and Johnston to the conclusion that the activation energy is not associated with the production of conduction electrons, but rather with the transfer of positive holes in the lattices

$$M^{3+}\text{—O—}M^{2+}\rightarrow M^{2+}\text{—O—}M^{3+}$$

This causes a transfer of local strains in the lattice. Some support for this interpretation is derived from the fact that Young's modulus for CoO is also found to undergo a large increase in passing through the Curie temperature.

It is interesting that the system $Li_xCu_{1-x}O$ appears to fall in line so neatly with the others. The structure of CuO is completely different from the sodium chloride structure in having the metal ion in a square planar coordination with oxygen. The very low concentrations of lithium permitted in this lattice make it difficult to find experimental evidence for the nature of the substitution. Indeed, it must be said that in all of these systems in the range over which systematic changes in electrical and magnetic properties occur, we are dealing with rather low concentration of impurities and that uenquivocal data on cationic environments are not yet available.

More complex phases of this type have been prepared by Johnston, Miller, and Mazelsky (90) in which more than one transition metal is present. Mixed oxides $Co_yNi_{1-y}O$, prepared by heating mixtures of cobalt and nickel oxides (11), were heated with appropriate quantities of lithium peroxide to give phases of composition $Li_x(Co_y\text{-}Ni_{1-y})_{1-x}O$. In a similar fashion, phases containing Mn + Co, Ni + Zn were obtained. The systems $Co_yNi_{1-y}O$, $Co_yMn_{1-y}O$ show a linear dependence of lattice constant with composition from $0 < y < 1$, while in the case of $Zn_yNi_{1-y}O$ it is linear over the range of homogeneity $0 < y < 0.28$ (upper limit of $y = .35$ according to Rigamonti (146)).

Particular attention was given to the phase $Li_x(Co_yNi_{1-y})_{1-x}O$. The variation of lattice parameter with y at constant x gave a minimum at room temperature and below at approximately $y = x$. At higher temperatures, the dependence is essentially linear. The conclusion is that at low temperatures the cobalt ion is preferentially oxidized, and that the formula could be represented as $Li_xCo^{3+}_{x}{}_{(1-x)}\text{-}Ni^{3+}_{xa}Co^{2+}_{y}{}_{(1-x)-x(1-a)}Ni^{2+}_{(1-y)(1-x)-ax}O$, where a is a distribution factor having the value 0.02 at −150°C., 0.37 at room temperatures, and 0.79 at 1000°C.

The phases with $x = .08$; $0.5 < y < .94$ appeared to have a tetragonal distortion which decreased with decreasing values of y. Attempts to prepare $Li_{.5}Co_{.25}Ni_{.25}O$ gave two phases, one with the rock salt structure ($a = 4.1012$ A.) and the other with $CsICl_2$ structure. The compositions of these phases were not determined, but it is suspected that partition of the cobalt and nickel occurs to some extent. $Li_{.5}Mn_{.25}Co_{.25}O$, on the other hand, gave a product which was predominantly a rock salt structure ($a \sim 4.15$ A.) but also contained a phase having the $CsICl_2$ structure, the lattice parameters of which are larger than those of $Li_{.5}Co_{.5}O$.

It is obviously impossible to account for these phenomena on the basis of ionic radii. Orientational forces, whether due to crystal fields or to covalent bond formation, must be playing an important role in imposing limitations on the compositions of phases of this type.

Among all the systems which can be regarded as related to the sodium chloride structure, only $LiTiO_2$ appears to have a completely random arrangement of the cations. $LiVO_2$, $LiCrO_2$, and $LiNiO_2$ have the layer-type structure. The atomic arrangements in $LiMnO_2$ and $LiFeO_2$ have not yet been established.

III. Mixed Oxides of the Spinel Type

Three binary oxides having the type formula M_3O_4 have the spinel structure which, like the sodium chloride structure, may be described in terms of oxide ions in a close-packed cubic arrangement. One-half of the octahedral cavities (B sites) and one-eighth of the tetrahedral cavities (A sites) are occupied by cations having the requisite valence to neutralize the charge of the oxide ions. The unit cell formula is $A_8B_{16}O_{32}$, where A and B represent the different cation sites. If the B sites are occupied by one kind of ion only, the structure is referred to as a normal spinel. Co_3O_4 is thought to be of this type and may be written $[Co_8^{2+}]_A[Co_{16}^{3+}]_BO_{32}$, whereas in Fe_3O_4 the ferric ion is distributed over A and B sites, $[Fe_8{}^{3+}]_A[Fe_8{}^{3+}Fe_8{}^{2+}]_BO_{32}$, and is called an inverse spinel. A simple representation of the spinel structure is given in Figure 6, which shows that the cations in the A and B sites lie close to one another and that electron transfer should not be prohibitive. Slight gains in lattice energy, which could accrue from special arrangements of the divalent and trivalent ions, could thus occur readily in these systems. Since we are accustomed to regard Co^{3+} and Fe^{2+} as especially favorable ions for octahedral coordination, it seems reasonable that the low temperature electron distribution in these oxides would be with Fe^{2+} and Co^{3+} in the B sites. In this way, the inverse structure of Fe_3O_4 and the normal structure of Co_3O_4 may be rationalized.

Mn_3O_4 differs from these oxides in having tetragonal symmetry ($a = 8.15$ A.; $c = 9.44$ A.). This distortion may be explained also

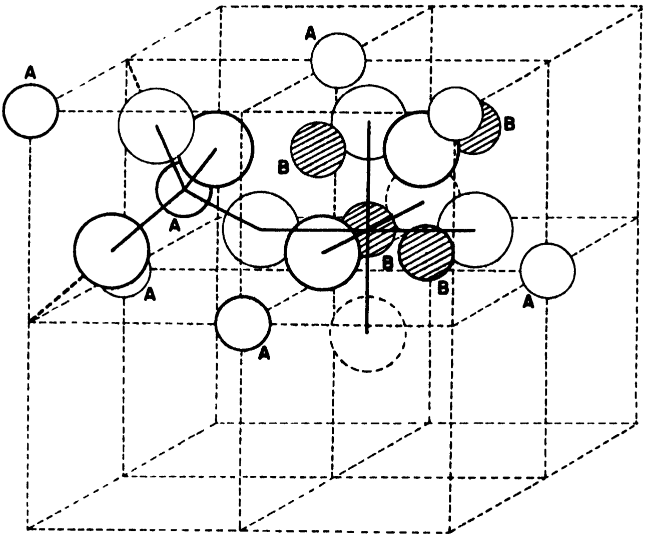


Fig. 6. The spinel structure. The total cube represents the unit cell of the spinel structure; *A* and *B* are the cations in tetrahedral and octahedral sites, respectively.

on the basis of a tendency toward covalent bond formation. Mn^{3+} should be especially suitable for the formation of dsp^2-type bonding. The octahedral sites would be more favorable geometrically for this than would the tetrahedral sites. The shortening of the Mn–O bonds in the 100 plane of the crystal could lead to the tetragonal distortion observed. Hence, Mn_3O_4 should be a normal spinel.

The theoretical interpretation of the magnetic and semiconducting properties of spinel-type compounds leans heavily on the crystallographic sites assigned to the cations. The practical application of this theory becomes important in the mixed oxides containing more than one metallic element. In this case, the cations have to remain in the sites adopted at the annealing temperature where ionic mobility is still appreciable. Gorter (71) lists 29 ions (all having radii between 0.5 and 1 A.) of 22 elements which are known to occur in spinel-like oxides. For each of these, tendencies for the adoption of tetrahedral or octahedral sites have been estimated. The influence of ionic size and charge appears to be that the larger ions with low charge and the small ions with large charge tend to occupy tetrahedral sites; the larger ions with high charge, octahedral sites. Specific tendencies are apparently associated with colvalent bond formation. Ions of all kinds, excepting those of the lanthanide or actinide elements, have been found as constituents of phases with the spinel structure. The following ions have radii suitable for inclusion in the spinel structure:

1. Noble gas-type ions: Li^+, Mg^{2+}, $Al^{3+}Na^+$, (Ca^{2+})
2. Transition metal ions
    a. 4th period: (Sc^{3+}), Ti^{4+}, V^{4+}, Cr^{3+}, Mn^{2+}, Mn^{3+}, Mn^{4+}. Fe^{2+}, Fe^{3+}, Co^{2+}, Co^{3+}, Ni^{2+}, Cu^+, Cu^{2+}, [Ti^{3+}], [V^{5+}]
    b. 5th period: Mo^{6+}, Rh^{3+}, Ag^+, [Nb^{5+}], [Ru^{4+}]
    c. 6th period: W^{6+}, [Ta^{5+}]. [Ir^{4+}], [Pt^{4+}]
3. Post-transition metals: $\underline{Zn^{2+}}$, $\underline{Cd^{2+}}$, $\underline{Ga^{3+}}$, $\underline{In^{3+}}$, $\underline{Ge^{4+}}$, Sn^{4+}

The ions enclosed in parentheses have been obtained only as minor substituents. Lithium may be partly replaced by sodium, magnesium by calcium, and iron(III) by scandium. The ions in square brackets have not been found in spinel structures. The likelihood of the compound Fe_2TiO_4 being actually $Fe^{2+}Fe^{3+}Ti^{3+}O_4$ is questioned by Gorter (71) on the ground that compounds such as M^{2+}-$Ti_2^{3+}O_4$ ($M = Mn, Co, Ni$) could not be prepared. Ions set in italics have been found to prefer octahedral sites. These are the ions with strong tendencies to form d^2sp^3 bonds (Cr^{3+}, Co^{3+}, Fe^{2+}) or dsp^2 bonds (Ni^{2+}, Cu^{2+}, Mn^{3+}). The fact that many spinels containing Ni^{2+}, Cu^{2+}, or Mn^{3+} are distorted to tetragonal symmetry appears to support this idea. The underlined ions tend to take up the tetrahedral sites, presumably due to the tendency toward sp^3 bonding since all of them are post-transition metals. Tin(IV) is the exception here, but octahedral coordination is the usual one for this ion in hydroxy stannates. The other ions listed do not appear to offer very strong competition for either site. The formula for phases with the spinel structure is not necessarily restricted to a 2:1 ratio of different kinds of ions. Possible formulas for phases with the spinel structure are listed in Table I. The cation valence combinations which have been found so far are 1–3, 1–4, 2–3, 2–4, and 1–6. The only examples of the 1–6 combination appear to be some molybdates and tungstates in which the hexavalent element is in the tetrahedral position and the univalent cation, Ag^+ or Na^+, in octahedral sites (44). This would appear to be contrary to expectations, since the octahedral coordination is a very usual one for Mo^{VI} and W^{VI}. It is possible, how-

TABLE I
Possible Formulas for Phases Having the Spinel Structure

Valence of cations	Formula	Examples
1,3	$M_4^{I}M_{20}^{III}O_{32}$	$LiFe_5O_8$ $LiAl_5O_8$
1,4	$M_{10^2/_3}^{I}M_{13^1/_3}^{IV}O_{32}$	$Li_{10^2/_3}Ti_{13^1/_3}O_{32}$
1,5	$M_{14}^{I}M_{10}^{V}O_{32}$	
1,6	$M_{16}^{I}M_8^{VI}O_{32}$	Ag_2MoO_4
2,3	$M_8^{II}M_{16}^{III}O_{32}$	$ZnFe_2O_4$
2,4	$M_{16}^{II}M_8^{IV}O_{32}$	Zn_2SnO_4 (inverse) $GeFe_2O_4$ (normal)
2,5	$M_{18^2/_3}^{II}M_{5^1/_3}^{V}O_{32}$	
2,6	$M_{20}^{II}M_4^{VI}O_{32}$	
2,3,4		$Ni_{12}^{II}Fe_8^{III}Ti_4^{IV}O_{32}$ (70)

ever, that the large size and the tendency of Ag^+ to form linear *sp*-bonds make the octahedral site more suitable, and it is perhaps significant that the oxygen octahedra containing the silver ions are not quite regular while the tetrahedra containing the Mo(VI) are regular. The sodium salts, however, have been found to be isotypic (111).

The distribution of ions in the various sites in a 2–3–4 spinel is said to be $[Fe_{5.6}Ti_{2.4})_A[Ni_{12}Fe_{2.4}Ti_{1.6}]_BO_{32}$ (72). This illustrates the strong tendency of Ni^{2+} to occupy octahedral sites, but the displacement of Ti^{4+} from octahedral sites by Fe^{3+} would not be predicted from the usual behavior of these ions.

The distribution of cations must obviously be somewhat temperature dependent, and a considerable amount of disorder would be expected in phases quenched from high temperatures. The 1–3 spinel $LiFe_5O_8$ has been shown by single crystal X-ray study to have the ordered structure $[Fe_8^{3+}]_A[Li_4Fe_{12}^{3}]_BO_{32}$ in which the lithium ions in oxygen octahedra somewhat elongated along the trigonal axis, are surrounded by six iron atoms. Above 755°C., however, the distribution apparently becomes random; at least the long-range order revealed by the diffraction pattern disappears (24).

More or less random distributions of cations have been demonstrated in the case of $CoFe_2O_4$ (189) and $MnAl_2O_4$ (77), the tendency being toward the inverse spinel. $MgGa_2O_4$ prepared at 1200°C. has been shown by X-ray analysis to have a more or less statistical distribution of cations (88). $NiAl_2O_4$, on the other hand, is almost completely of the inverse type (77,147), while $FeAl_2O_4$, $CoAl_2O_4$, and $ZnAl_2O_4$ are of the normal type.

Since the magnetic characteristics and the electrical conductivity of phases of this kind are strongly dependent upon the positions adopted by the cations, it has been important to discover means of controlling this factor by using cations with marked coordination tendencies. To this end, many systems involving two or more spinels have been studied. These are commonly regarded as solid solutions between the end members. $CoAl_2O_4$ and $ZnAl_2O_4$, for example, give a continuous series of solid solutions in which the lattice parameter is a linear function of the composition (147).

The variation of lattice parameter caused by cationic substitution may give information about the cation distribution in some instances. With the system Co_2TiO_4–Zn_2TiO_4, Romeijn found that the lattice parameter remains essentially constant from Co_2TiO_4 to $CoZnTiO_4$. Further substitution of zinc causes a substantial increase in lattice constant. This can be understood if we assume that the cobalt compound is an inverse spinel, $Co(TiCo)O_4$ (the B cations are in parentheses), the first substitution of zinc occurring in the A position to give $Zn(TiCo)O_4$. Subsequent addition of zinc must occur in the octahedral sites. A similar instance of this has been found with germanium substitution (45). $Fe^{3+}(Fe^{2+}Fe^{3+})O_4$ and $Ge(Fe_2)O_4$ form a continuous series of solid solutions, the lattice parameter remaining constant over the entire range. In the system $Fe(NiFe)O_4$–$Ge(Ni_2)O_4$ a linear variation of lattice parameter with composition was found. A more complex example of multiple substitution is the system $MgFe_2O_4$–$GeCo_2O_4$. While the magnesium iron oxide is commonly regarded as an inverse spinel, it has been shown by Gorter (73) and by Pauthenet and Bochirol (135) that the cation distribution is somewhat random and may be indicated by the formula $Fe_{1-x}Mg_x(Fe_{1+x}Mg_{1-x})O_4$, where x increases with temperature according to the expression $x(1 + x)/(1 - x^2) = \exp(-E/kT)$. With simultaneous substitution of Ge^{4+} and Co^{2+} for Mg^{2+} and Fe^{3+} the germanium would be expected to adopt the tetrahedral sites. The lattice constant variation which accompanies this substitution has a minimum at the composition $^3/_4$ $Mg\ Fe_2O_4$–$^1/_4$ $GeCo_2O_4$. This could be explained if it is assumed that at the temperature of preparation one-fourth of the magnesium is in the A sites and that the germanium preferentially displaces the magnesium. The formula for the solid solution of minimum lattice constant would then be $Ge_{1/4}Fe_{3/4}(Mg_{3/4}Fe_{3/4}Co_{1/2})O_4$. The value of $x = {}^1/_4$ is not an unreasonable figure for the randomness of the magnesium ion.

Not all of the systems display a complete range of homogeneity. An immiscibility gap occurs in the $Ge_xMg_{1-x}(Co_{2x}Fe_{2-2x})O_4$ system between ${}^1/_2 < x < {}^7/_8$ and in the system $(Ge_xZn_{1-x})(Co_{2x}Fe_{2-2x})O_4$ from ${}^1/_2 < x < 1$, which may be associated with the absence in these systems of any cation with strong tendency toward octahedral coordination. The failure to obtain solid solutions, however, may be due to the tendency to form other phases under the severe conditions required for reaction between solids. It has been found, for example, that $GeMg_2O_4$ can only be synthesized as a spinel below 900°C., at which temperature transformation to the olivine (Mg_2SiO_4) structure occurs, and that $GeCo_{2-x}Mg_xO_4$ phases have the olivine structure when $x > 0.15$ upon annealing at 950°C. (45).

Distorted and regular spinels may also show immiscibility gaps at low temperatures. Mixed spinels of Mn_3O_4 and Fe_3O_4 have been made by heating mixtures of the oxides in sealed tubes. A complete series of solid solutions is obtained only above 1160°C. (194), which is the temperature of the tetragonal → cubic transition of Mn_3O_4. An immiscibility gap develops below this temperature widening with decrease in temperature. The homogeneous phase presumably has the structure $Fe^{3+}_{1-x}Mn^{2+}_x(Fe^{2+}_{1-x}Mn^{3+}_{2x}Fe^{3+}_{1-x})O_4$.

The reaction of equimolar mixtures of FeO and Mn_2O_3 at 900°C. followed by quenching gave a substance with a tetragonally distorted spinel structure $c/a = 1.05$ (170), whereas a similar phase in the cobalt–manganese system has $c/a = 1.12$. To explain this difference in distortion, it is suggested that in the manganese–iron phase an electron transfer

$$Mn^{3+} + Fe^{2+} \longrightarrow Mn^{2+} + Fe^{3+}$$

occurs and that the compound should be represented as $Fe^{3+}_{0.5}Mn^{2+}_{0.5}(Fe^{2+}_{0.5}Mn^{3+}_{1.5})O_4$; whereas the cobalt compound is $Co^{2+}(Mn^{3+}_2)O_4$, the greater proportion of Mn^{3+} causing a larger distortion of the oxygen octahedra.

It is obvious that the product is likely to vary with the conditions of preparation. The minimum temperature required for sintering many of these phases is about 1300°C., and reliable physical measurements can only be obtained with well-sintered specimens. According to Gorter (74), the compound $MnFe_2O_4$ under these circumstances yields a phase containing trivalent maganese $Mn^{2+}_{1+a}Fe^{3+}_{2+6a}Mn^{3+}_{2a}O_{4+13a}$ in which the oxygen to metal ratio is somewhat less than 4:3. It has been shown that above 1050°C. a spinel phase containing as much as 10% Mn^{3+} is formed. Annealing at lower temperatures caused a separation into Mn_2O_3 and Fe_2O_3. Application of the phase rule to these systems presents some difficulties, as has been demonstrated by a study of the system

$$2\ Fe_3O_4 + {}^1/_2\ O_2 \rightleftharpoons 3\ Fe_2O_3$$

Flood and Hill (53) found that the data could be interpreted by the phase rule only if an expression for crystal defects were included in the range where a single phase exists.

The deviation from stoichiometry of many phases with the spinel structure occurs with systems in which oxidation may occur or in which an ion of higher valence can be substituted for one of lower valence. A nickel-iron oxide, having the approximate composition $\cdot 2NiO{:}\cdot 8Fe_2O_3$, for example, has the spinel structure (85). This should probably be construed as $Fe^{3+}(Ni^{2+}_{.38}Fe^{2+}_{.23}\ Fe^{3+}_{1.26})O_4$ with 0.13 cation vacancy per unit cell, for the weight of evidence appears to indicate that the defects consist of cation vacancies in the B positions (171). Verwey (200) has pointed out that, contrary to systems like NiO, lattice defects in Fe_3O_4 caused by oxidation lead to decrease in electrical conductivity. Stoichiometric Fe_3O_4 exhibits a kind of transition reflected in a rapid rise in resistivity as the temperature falls below 120°K. This is associated with an ordering of the conduction electrons (the Fe^{2+} ions) about the sixteenfold positions. With an oxide of composition which could be represented as $Fe^{3+}(Fe^{2+}_{.95}\square_{.02}Fe^{3+}_{1.03})O_4$, the resistance increases about ten-fold, the transition temperature is lowered to about 100°K., and the increase in resistance at this point becomes very small. These phenomena are explained as being due to the presence of "frozen in" random cation vacancies around which the Fe^{3+} ions in the octahedral positions tend to congregate, thus inhibiting the ordered distribution of electrons.

The range of composition over which the spinel structure exists in phases produced by heating Fe_2O_3 in nitrogen at 1300°C. is not large, and hence it has been rather puzzling that γ-ferric oxide should have the defect spinel structure $Fe^{3+}_8(Fe^{3+}_{13{}^1/_3}\square_{4{}^2/_3})O_{32}$.

The preparation of γ-ferric oxide is effected by the thermal decomposition of some hydrous iron(III) oxides at low temperatures. It was also reported to form by the careful oxidation of Fe_3O_4 at low temperatures (208). It has been generally accepted that γ-ferric oxide has the spinel structure. Re-examination of this phase (41, 195), however, has shown that γ-ferric oxide always contains the elements of water. David and Welch clearly showed that magnetite prepared by a dry method did not yield any detectable quantity of the γ-ferric oxide upon oxidation between 185 and 370°C. but that magnetite prepared from solution gave the γ-oxide on oxidation at temperatures from 180 to 500°C. The product always contained a small amount of water, approximately 0.5–1%. A striking similarity was observed in the X-ray diffraction pattern of γ-ferric oxide and $LiFe_5O_8$, and by analogy David and Welch suggest that the structure may lie between $Fe_8^{3+}(Fe_{12}^{3+}\square_4)(OH)_4O_{28}$ and $Fe_8^{3+}(Fe_{13^1/_3}^{3+}\square_{2^2/_3})O_{32}$, where the square represents a cation vacancy. Van Oosterhout and Rooijmans come to a somewhat similar conclusion, but propose Fe_8^{3+}-$[(H_4)Fe_{12}^{3+}]O_{32}$ and $Fe_8^{3+}[(Fe_{1^1/_3}^{3+}\square_{2^2/_3})Fe_{12}]O_{32}$, where the ions within the square brackets are in the octahedral sites and those in parentheses distributed randomly in the positions of the four lithium atoms in the ordered ferrite. A tetragonal cell $c/a = 3$; $a = 8.33$ A.) is proposed for γ-ferric oxide.

The stabilization of γ-ferric oxide by heating with sodium hydroxide is explained by the assumption that the sodium ions fill the vacancies in the lattice (186).

Deviation from stoichiometry in spinel-like compounds by introducing anion deficiencies or interstitial cations does not appear to be clearly established. From the data of Verwey and Haayman (200) a product obtained by reduction of ferric oxide to a composition representing at the most an oxygen deficiency of less than 0.1 oxygen per unit cell of the spinel structure showed the presence of FeO under examination by X-rays. The lattice constant of the spinel phase was not appreciably different from that of stoichiometric Fe_3O_4.

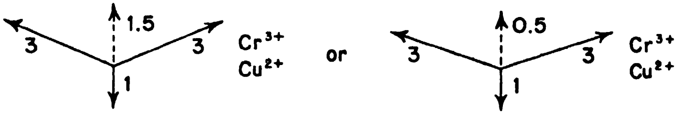
Much information has been obtained about the distribution of cations in phases with the spinel structure from saturation magnetization measurements. The theory of superexchange in oxides indicates that the strongest interaction should occur between A cations and their neighboring B cations. For Fe_3O_4 (see Fig. 6), Fe_A–O = 1.88 A., Fe_B–O = 2.03 A., and the angle Fe_B–O–Fe_A = 125° may be compared to the most favorable situations for AA interaction, Fe_A–O = 1.88 A., Fe_A–O = 3.46 A., and angle Fe_A–O–Fe_A = 80°, or, for BB interaction, Fe_B–O = 1.88 A., and angle Fe_B–O–Fe_B = 93.5°. Thus the spins of the B cations should be opposed to those of the A cations

$$\underset{\leftarrow}{Fe^{3+}}\ (\underset{\rightarrow}{Fe^{2+}}\ \underset{\rightarrow}{Fe^{2+}})O_4$$

and the system can be regarded as consisting of two sublattices, one of the B cation and the other of the A cation. Upon the assumption that each sublattice is saturated—that is, all the spins within the lattice are parallel—the resultant moment would be due to the four unpaired electrons of Fe^{2+} in the B sites which corresponds with the experimental value $4.1\mu_B$ per formula weight. Several of these magnetic structures have been confirmed by neutron diffraction studies (39,86, 167). Deviation of experimental values of saturation moments from those predicted in this way occur in several instances. The copper-iron spinel has been shown to be virtually completely inverse (136) with no ordering of the copper ions in the B sites. On this basis one would expect a saturation moment (M_{sat}) of 1.0 μ_B. The experimental value is higher than this and depends upon the temperature of preparation and rate of cooling. This is taken as an indication of distribution of some Cu^{2+} ions in A sites similar to the case of $Mg_xFe_{1-x}(Fe_{1+x}Mg_{1-x})O_4$. The value given by Gorter is 1.3 μ_B, which corresponds to about 4% Cu^{2+} in the A sites. This explanation seems valid in view of the facts that $CuFe_2O_4$ undergoes a transition from tetragonal (the inverse form) to cubic (presumably a random form) at about 760°C. (178) and the cubic form has a higher magnetic saturation than the tetragonal form. Other phases which have larger magnetic saturation than the predicted values, the inverse spinels $Fe(CoFe)O_4$ (3.7 μ_B) and $Fe(NiFe)O_4$ (2.3 μ_B), but which do not change with different quenching conditions, are explained on the assumption that there is in each case an orbital contribution for Ni^{2+} and Co^{2+} (75).

An interesting system involving the transition from an inverse to a normal spinel structure is provided by $Fe^{3+}_{1-x}Zn_x(Ni_{1-x}Fe^{3+}_{1+x})O_4$. The M_{sat} vs. x curve is linear up to $x = .4$, the value of M_{sat} being close to the expected value, 5.2 μ_B. For higher values of x, however, the AB interaction is apparently diluted sufficiently so that the spins of the ions in the A and B sublattices are no longer parallel, and the observed moment is smaller than predicted on the simple additive rule. With $x = 1$ the phase becomes completely antiferromagnetic.

In contrast to the copper-iron spinel, the copper-chromium spinel has been found to be of the normal type (136), the tetragonal distortion ($c/a = 0.91$) being attributed to a flattening of the oxygen tetrahedra around the copper ions as if there were some tendency toward a square-bond formation. The predicted moment would be 5 μ_B whether copper were covalently bonded or not. The observed moment is 0.51 μ_B at 77°K. From the magnetic peaks observed in the neutron diffraction pattern, Prince (137) deduces that the spins of the Cr^{3+} ions in the same 001 layer are all parallel but are oriented at an angle in adjacent layers. The resultant moment of the Cr^{3+} ions may be either 1.5 or 0.5 μ_B instead of 5 μ_B.



Low experimental values for M_{sat} for the system $Co_{1-x}Zn_x(Co_2)O_4$ have led Cossee (40) to suggest that the Co^{3+} ion in octahedral sites is covalently bonded and hence makes no contribution to the magnetic moment. It seems inconsistent to grant Co^{3+} the power of covalency and to withhold it from Fe^{2+}.

It is evident from these examples that, while theoretical explanations for observed physical and chemical properties can usually be given, it is not always possible to make precise predictions about the properties in specific cases.

IV. Stabilized Spinel Structures of the Magnetoplumbite Type

The chemical composition of a specimen of the mineral magnetoplumbite has been given as $Pb_2(Fe_{15}Mn_7AlTi)O_{38}$ (11). It has a hexagonal structure ($a = 5.88$ A.; $c = 23.02$ A.). Isomorphous with this mineral is $BaFe_{12}O_{19}$, a substance with remarkable magnetic properties which may readily be prepared by heating the stoichiometric quantities of barium carbonate and ferric oxide in air (49) above 750°C. The structure was first determined by Adelsköld (1) and offers an example of the deduction of the correct formula from structure determination in absence of reliable chemical analyses.

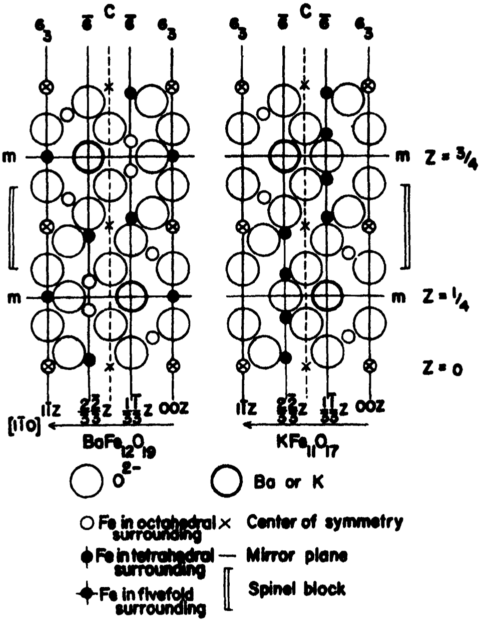


Fig. 7. A comparison of the structures of $BaFe_{12}O_{19}$ and $KFe_{11}O_{17}$.

The structure may be visualized as layers of a spinel structure separated by layers of barium, iron, and oxide ions. In the spinel region four layers of cubic close-packed oxygen ions lie in infinite planes normal to the *c* axis, and the Fe^{3+} ions occupy positions equivalent to those in the spinel structure. The barium-iron-oxygen layer is a single plane of oxygen atoms in which one of four oxygens is replaced by barium ions in such a way that triangles of oxygens are formed, half of which contains the iron atoms. The adjacent layers of oxygens in the contiguous spinel plates lie in such a way that these iron atoms are in a five-fold trigonal bipyramid coordination with oxygen and the barium ions in a hexagonal close-packed twelve-fold coordination with oxygen.

The structure of the compounds $KFe_{11}O_{17}$ and, $KAl_{11}O_{17}$ is very similar. The comparison given in Figure 7 shows that they differ only in the layer connecting the spinel-like sheets. The composition of the layer in the unit cell of $KFe_{11}O_{17}$ is KO, whereas it is $BaFeO_3$ in the barium compound. The potassium compound is antiferromagnetic, while the barium compound is strongly ferromagnetic with the preferred direction of magnetization along the *c* axis. This striking difference is due to the difference in the layers connecting the spinel-like sheets.

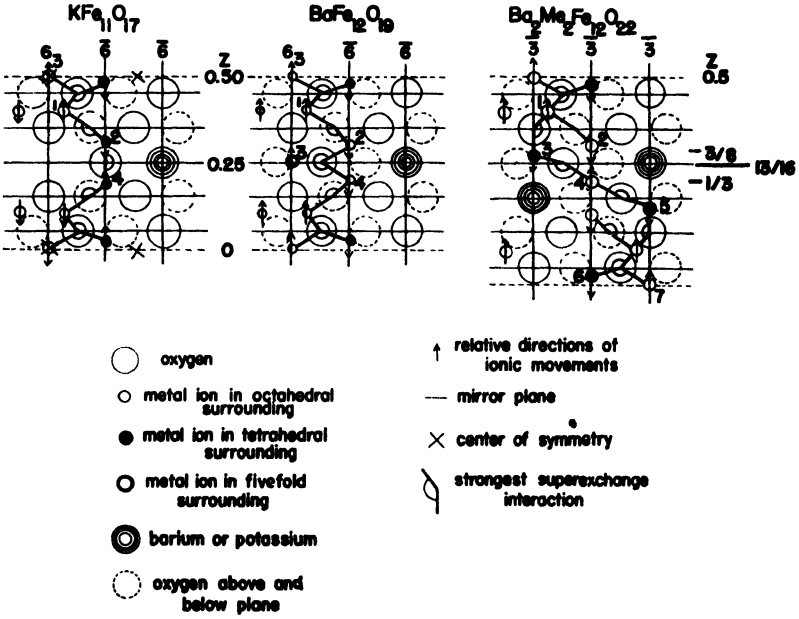
In the course of preparation of single crystals of $BaFe_{12}O_{19}$ from molten mixtures of barium and ferric oxides in an oxygen atmosphere, the presence of other closely related phases was detected (25). These phases were found to be related to each other in a manner which seems to be typical of layer structures such as have been found in so-called basic chlorides of zinc, magnesium, and cadmium or in the series of phases between $Mg(OH)_2$ and Mg_2SiO_4 in which portions of the layer structures are identical, but the sequence differs. All of the new barium iron oxide phases characterized by Braun were found to contain small amounts of ferrous ion, and all of them were ferromagnetic. This proved to be important in recognition of pure phases, for it was possible to orient small crystallites in a plastic film. The diffraction patterns from these oriented crystals were easily distinguished in contrast to the ordinary X-ray powder diagrams which contained many overlapping lines (92). The new phases isolated in this way were, upon the basis of structural analysis, assigned the formulae $BaFe_2^{2+}Fe_{16}^{3+}O_{27}$ and $Ba_2Fe_2^{2+}Fe_{28}^{3+}O_{46}$. The presence of ferrous ion suggested the substitution of other divalent cations, and by heating mixtures of MO (M = Zn, Co) + BaO + Fe_2O_3 two other related phases, $Ba_2Zn_2Fe_{12}^{3+}O_{22}$ and $Ba_3Co_4^{2+}O_{41}$, were isolated. Only a general description of the structures deduced by Braun for these compounds can be given here. The spinel-like layers are found to be of two kinds, one consisting of four layers of cubic close-packed oxygens (S_4) and the other of six layers (S_6). Two kinds of barium-iron-oxygen layers were also found, the single layer (B_1) already described and a double layer (B_2) in which the barium ion in one layer overlies the iron ion in the other, causing a displacement of the iron from its five-fold position to a tetrahedral environment. The compounds are listed in Table II in order of decreasing M/Ba ratio (where M represents iron, zinc, and cobalt). The *c* axes vary over a considerable range, but the *A* axis is the same (~5.9 A.) for all sequences of the different kinds of layers.

It will be observed that there are no B_2 layers where there are S_6 layers. The small divalent cations in these phases may be Mn, Fe, Co, Ni, Zn, or Mg, except perhaps in compound 2 for which no substitutions are listed by Jonker *et al.* (92). As Braun has observed, it

TABLE II
Structures of Compounds Related to Magnetoplumbite

	Formula	Layer sequence	*c* axis, A.
1.	$BaFe_2^{2+}Fe_{16}^{3+}O_{27}$	$-B_1-S_6-$	32.8
2.	$Ba_2Fe_2^{2+}Fe_{28}^{3+}O_{46}$	$-B_1-S_6-B_1-S_4-$	84.1
3.	$BaFe_{12}O_{19}$	$-B_1-S_4-$	23.2
4.	$Ba_3Co_2^{2+}Fe_{24}^{2+}O_{41}$	$-B_1-S_4-B_1-S_4-B_2-S_4-$	52.3
5.	$Ba_2Zn_2Fe_{12}^{3+}O_{22}$	$-B_2-S_4-B_2-S_4-$	43.6

is strange that random sequences of layers are not found. The crystal habit is a plate-like crystal, the growth occurring predominantly normal to the *c* axis. Gorter (75) has given an interpretation of the magnetic properties of compounds 1, 3, 4, and 5 and of $KFe_{11}O_{17}$ on the



$KFe_{11}O_{17}$
$BaFe_{12}O_{19}$
$Ba_2Me_2Fe_{12}O_{22}$
6_3
$\bar{6}$
$\bar{6}$
$\bar{3}$
z
0.50
0.25
0
0.5
−3/8
−1/8
13/16
1
2
3
4
5
6
7
oxygen
metal ion in octahedral surrounding
metal ion in tetrahedral surrounding
metal ion in fivefold surrounding
barium or potassium
oxygen above and below plane
relative directions of ionic movements
mirror plane
center of symmetry
strongest superexchange interaction

Fig. 8. A comparison of the superexchange phenomenon in $KFe_{11}O_{17}$, $BaFe_{12}O_{19}$, and $Ba_2Me_2Fe_{12}O_{22}$.

basis of the superexchange theory. His diagrammatic representation is presented in Figure 8. It can be seen that negative interaction of the tetrahedrally surrounded iron atoms which lie adjacent to the

K—O layer in $KFe_{11}O_{17}$ causes the A sublattices of the adjacent spinel layer to have opposed spins, and hence the B sublattices are also opposed, leading to antiferromagnetism. On the other hand, the iron atom (five-fold) which lies in the Ba—O layer is situated very favorably relative to the two octahedrally surrounded iron atoms which lie between the Ba—O layer and the adjacent spinel layers. It is the negative interaction of these interlayer iron atoms with the iron atoms in the B sites which causes the parallel alignment of all of the B cations. The A cations are therefore antiparallel by AB interaction. The saturation magnetization calculated on this basis (20 μ_b) agrees perfectly with the experimental data.

The saturation magnetization of compounds of type 5 containing Mg, Co, or Ni agrees with values predicted on the basis of a statistical distribution of the divalent ion over all octahedral sites.

The preferred direction of magnetization of many of these crystals is parallel to the *c* axis. The magnetic anisotropy is very large in the case of $BaFe_{12}O_{19}$ so that it is practically impossible to demagnetize a sintered aggregate of oriented crystals. The preparation of oriented, sintered ceramics of $BaFe_{12}O_{19}$ is discussed by Stuijts (182).

It has been found that with all of the phases having the structure of compound 5, the preferred direction of magnetization lies in the plane normal to the *c* axis, but that essentially free rotation may occur in this plane. This property is also found in the cobalt compounds of types 1 and 4. Because of this phenomenon, these phases prove to be superior to the ferromagnetic spinel phases for soft magnetic core materials in retaining a high initial permeability to much higher frequencies.

The development of the chemistry of phases of this kind is following lines similar to those used in the exploitation systems of the spinel type, with the principal interest centering on the magnetic properties. The system $BaM^{2+}_{2-x}Zn_xFe_{16}O_{27}$ (where M = Fe (75), Co (197)) shows variations in saturation moments with x similar to those found with the corresponding spinel structure. The substitution of trivalent cations for Fe^{3+} and of divalent cations for Ba^{2+} in $BaFe_{12}O_{19}$ has been investigated to some extent (196). Lead and strontium may completely replace the barium, but with calcium only a partial substitution can be made. Al^{3+}, Ga^{3+}, Ge^{3+}, Mn^{3+}, and Cr^{3+} may replace part of the iron. The ferromagnetic resonance frequencies and coercive forces were found to reach very high values in some products in the system $BaFe_{12-x}Al_xO_{19}$. Brisi and Burdese (26) found that the limit of substitution of Cr^{3+} was about 50 mole % of the iron. Some rare earth ions may partially replace barium in the compound, apparently with a compensating decrease in valence of some of the iron. Up to 0.7 mole fraction of lanthanum can be introduced, but the substitution limits drop sharply to 0.1 mole fraction for samarium and europium (42). The major lattice parameter change is a decrease in the *c* axis. The barium may also be replaced by combinations of alkali metals and rare earths (184).

It is clear that numerous possibilities exist for further variations in the composition of these layer lattice phases. The composition of magnetoplumbite suggests that combinations of di- and tetravalent ions may be substituted for Fe^{3+}. Perhaps this kind of substitution has been effected by the introduction of germanium. The highest mole fraction of divalent ions found in the spinel layers of these compounds is $^1/_7$ if we can assume that all of the Fe^{2+} ions lie in this region; whereas it is $^1/_3$ in the 2–3 spinel structure. It is not known whether this is an incidental matter or whether it is a necessary feature of the structure.

V. Mixed Oxides of the M_2O_3 Group

The class of metallic oxides of general formula M_2O_3 has many representatives among the binary oxides. The most usual structural types are corundum (Al_2O_3) and the C and A rare earth structures. The corundum structure is adopted by the oxides of trivalent cations with radii suitable for six-fold octahedral coordination with oxide ions. The sesquioxides of gallium and the elements of the first transition period from titanium to iron (excepting manganese) and rhodium belong in this group. The structure may be described as a hexagonal close-packed arrangement of the oxide ions in which the cations are arranged symmetrically in two-thirds of the octahedral cavities. The coordination number of the cations in the C rare earth structure is also six, but two different environments are found, both of which can be described in terms of a cubic disposition of oxygen around the cation. In one, vacancies occur at the edge diagonal and in the other at the cube diagonal. The cations are in a cubic close-packed arrangement. The structure is thus similar to that of fluorite (CaF_2), but with ordered anion vacancies. The oxides of scandium, yttrium, the smaller rare earth ions from samarium to lutecium, and probably the trivalent actinide elements beyond plutonium have this structure, and the other rare earth oxides at high temperatures also appear in this form. The sesquioxides of the post-transition elements indium and thallium are other members of the group. The occurrence of Mn_2O_3 with this structure may be due to the tendency of Mn^{3+} to square-bond formation since the radius (0.62 A.) is so much less than those of the other cations (>0.8 A.) found in this structure. The coordination number of the cation with oxygen in the A rare earth structure is seven, six of the oxygens being in a distorted octahedral arrangement with the seventh adjacent to one face of the octahedron. At room temperatures M_2O_3 compounds of lanthanum to neodymium and actinium exhibit this atomic arrangement in hexagonal crystals.

Little interest has been shown in mixed oxides of the rare earth types, but considerable attention has been given to those with the corundum structure. The mineral ilmenite, $FeTiO_3$, is typical. The phenomena encountered in systems of this kind are very similar in character to those described for the spinel systems and will not be taken up in detail here. A discussion of the magnetic properties is given by Gorter (71). There does not appear to be any wide departure from stoichiometry in compounds of this type. Even the readily reducible or oxidizable Ti_2O_3 has a very narrow range of homogeneity, probably less than .02 atom % oxygen (113). Apparently, this structure does not lend itself to cation vacancies or to interstitial ions. With cations of different valence, the combination most often found appears to be 2 and 4, as in $MTiO_3$ (M = Mn, Co, Ni, Mg, Zn, Cd) although the combination 2-3-4 may be present in ilmenite itself. It would seem reasonable to propose the existence of phases of the types, $Mg_xM^{3+}_{2-2x}M^{4+}_xO_3$ or $Li_xM^{3+}_{2-3x}M^{4+}_{2x}O_3$, where M is a metal such as Ti, V, or Mn which may readily exist in both the +3 and +4 oxidation states. Such systems do not appear to have been investigated.

Sesquioxides such as Al_2O_3 and Fe_2O_3, when heated with small proportions of alkali hydroxides, are, however, readily converted to a spinel form. We have seen that higher concentrations of Li^+ lead to the $NaCrS_2$ structure with several trivalent transition metals and to the random NaCl structure with Ti^{3+}.

The inflexibility of the ilmenite structure is revealed in the systems $NiAl_2O_4$–Al_2O_3 (58) and Fe_2O_3–Mn_2O_3 (131). In the former, the

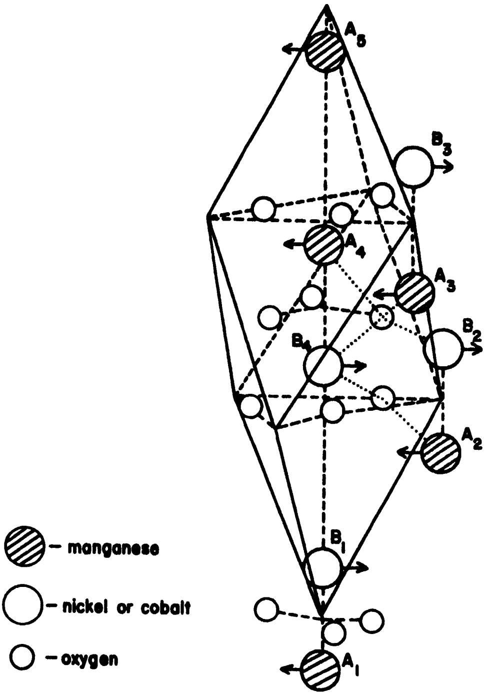


Fig. 9. The magnetic structure of the ilmenite phase $NiMnO_3$.

spinel structure apparently persists down to about 6 mole % $NiAl_2O_4$, while in the latter no solubility of Mn_2O_3 in Fe_2O_3 could be detected. The cubic Mn_2O_3, on the other hand, could take up as much as 60 mole % of Fe_2O_3 without change in structure.

The synthesis of two magnetic ternary oxides, $NiMnO_3$ and $CoMnO_3$, with the ilmenite structure has been carried out under hydrothermal conditions (185). The nickel compound was prepared from mixtures of NiO and MnO_2 in dilute NaOH solution at 700°C., the cobalt compound from CoO and MnO_2 in dilute H_2SO_4 solution at 625°C. The pressure was 3000 atmospheres. The crystal structure is shown in Figure 9 (34). The cations lie in planes normal to the three-fold axis of the rhombohedral cell, the manganese ions being in alternate planes. The structure is therefore very similar to that of $Na_{.5}Ni_{.5}O$, except that, in this case, the oxide ions are in close-packed hexagonal arrangement, and only two-thirds of the octahedral cavities contain metal ions. Magnetic measurements show that these compounds are ferrimagnetic. The strongest superexchange interactions probably occur in the configurations A_3—O—B_4 and A_2—O—B_4 and also A_3—O—B_2. If all of these interactions are negative, all metal atoms in the nickel or cobalt layer would have parallel spins and would be opposed to those of the manganese atoms in the adjacent layers. The fact that the direction of easy magnetization is in the direction of the planes of metal atoms is compatible with this picture.

VI. Mixed Oxides with the Perovskite Structure

The rare earth structures appear to be the result of an awkward compromise in the coordination tendencies of the cation and number of available anions. Interaction of these oxides and those of the ilmenite group leads to a much more favorable arrangement in which the rare earth cation is in twelve-fold coordination with oxygen and the other cation in six-fold octahedral coordination. The atomic arrangement which was first observed in the mineral perovskite, $CaTiO_3$, may be described in terms of a cubic close-packing of oxygen atoms, one quarter of which has been replaced by the large cation in a fashion similar to the Ba—O layer in the magnetoplumbite structure. The octahedral cavities formed by the oxygen atoms contain the

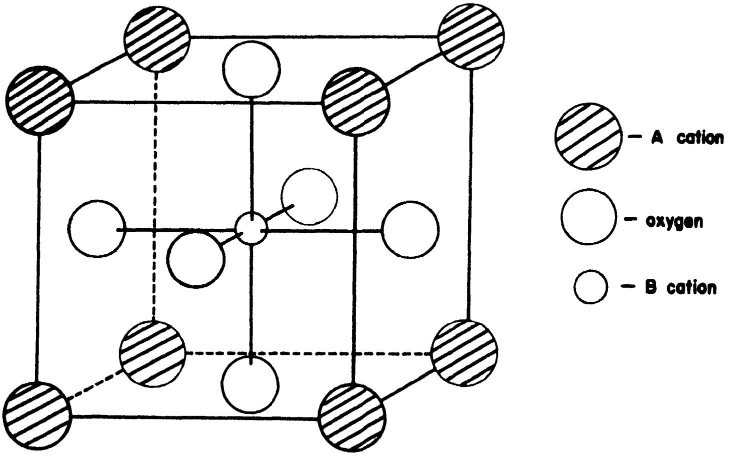


Fig. 10. The perovskite structure.

smaller cation. It is easier to visualize the atomic positions on the model of a cubic unit cell (Fig. 10), the corners of which are occupied by the large cation, the face-center positions by the oxygen, and the center by the small cation. Contrary to the convention used in the spinel structure, the A and B cation sites are for the large and small coordination numbers, respectively. In order to have complete contact of all nearest neighbors in this cubic structure, it is obvious that $R_A + R_O = [\sqrt{2}(R_B + R_O)]^{1/2}$, where R_A, R_B, and R_O are the ionic radii. Deviations from cubic symmetry would be expected when this relationship is not observed, but the general features of the structure are usually preserved when the tolerance factor (t)

$$t = \frac{R_A + R_O}{[\sqrt{2}(R_B + R_O)]^{1/2}}$$

lies in the range about 0.7–1.

An additional provision is, of course, that the A and B cations have sizes appropriate to twelve- and six-fold coordination with oxygen. The ratio R_A/R_O, which should be about unity for twelve-fold coordination, is not very critical. Megaw (128) has shown that the A–O distance in some perovskite-like compounds may be greater by about one-tenth than the sum of the radii. Among the divalent cations, cadmium has the smallest radius of any found in perovskite-type structures. At room temperatures $CdTiO_3$ (t = 0.81) has the ilmenite structure but changes to an orthorhombic modification of the perovskite structure at elevated temperatures. The radius of the calcium ion is about 2% greater than that of cadmium, yet $CaTiO_3$ (t = .81) appears to exist only in the perovskite structure. If ionic packing were the only criterion for structure determination, there must be a surprisingly critical limit to the size factor.

The lower limit for contact in an octahedral site formed by close-packed oxygen ions (R_O = 1.40 A.) should be 0.58 A. The aluminum ion (0.51 A.), however, forms perovskite-like compounds such as $LaAlO_3$ (t = .94). Other small cations, e.g., Ge^{4+} (0.53 A.) and V^{5+} (0.59 A.), are not found in structures of the type, even though the tolerance factor is favorable. $BaGeO_3$ (t = 1.00) has a silicate type of structure (pseudowollastonite) with the germanium in tetrahedral coordination (151). A similar kind of structure is found with vanadium in KVO_3 (t = 0.88) (50), although $NaNbO_3$ (t = 0.8) has the perovskite structure.

The difference in behavior of Al^{3+} and Ge^{4+} could be due to the greater tendency of the latter to form sp^3 bonds, but Wadsley has shown that coordination numbers of 5 and 6 are not incompatible with pentavalent vanadium (205).

Under the circumstances of preparation of these phases, it can be assumed that the atomic arrangement with the highest lattice energy will prevail. The perovskite structure is one of high lattice energy and is favored in many instances, but there are other arrangements of ions in ABO_3 compounds which are also described in terms of closest packing of A cations and oxide ions (the $BaNiO_3$ and the hexagonal barium titanate structures), which also must have high lattice energies. Further, there is no a priori reason why a stoichiometric mixture of A and B oxides should yield a compound of composition ABO_3. Other phases with different A/B ratios are frequently formed, and it is obviously a formidable problem to decide, on the basis of thermodynamics, which of inumerable A/B ratios would provide the lattice of highest energy. Consequently, in spite of its obvious shortcomings, it is usual to resort to a more or less empirical approach based on the assumption that ions have fixed dimensions and definite coordination tendencies.

The flexibility of the perovskite system of compounds arises because (*1*) the valence combinations of the A and B cations may be 3–3, 2–4, and 1–5 and (*2*) wide departures from stoichiometry involving both anion and cation vacancies may occur in some instances.

A. $A^{3+}B^{3+}O_3$ COMPOUNDS

The A cations in the 3–3 compounds appear to be invariably of the rare earth type. The B cations may be any of the fourth period transition elements from scandium to nickel, inclusive, and the Group III elements aluminum, gallium, and indium. Yttrium forms compounds of the type YBO_3, where B may be Al, Cr, Fe, and also the compound $LaYO_3$, where the yttrium occupies the B position (133).

The combination of yttrium or the smaller rare earth ions with some of the smaller B cations, notably Ga (100), Al (215), and Fe (12,64), tends to the formation of garnet-like phases in which yttrium has eight-fold coordination and the B cation both octahedral and tetrahedral coordination. The stoichiometry is different, namely, $Y_3Al_2(AlO_4)_3$. This type of phase appears to be formed only by

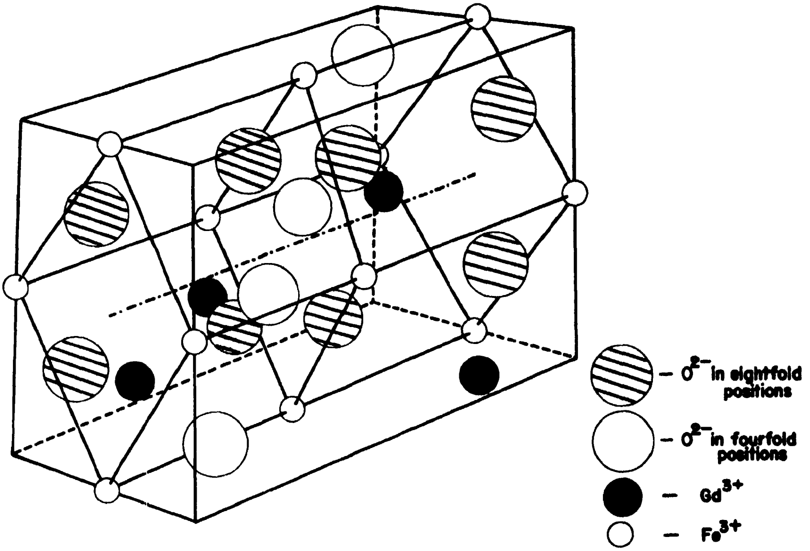

– O^{2-} in eightfold positions
– O^{2-} in fourfold positions
– Gd^{3+}
– Fe^{3+}

Fig. 11. The relationship of the orthorhombic unit cell to the perovskite structure.

those B cations which tend to tetrahedral bonding (Al, Ga) or which do not specifically prefer octahedral bonding (Fe^{3+}).

Parallel to the case of spinel-like compounds, the interpretation of physical characteristics of the perovskite-type compounds has called for a more precise knowledge of the atomic configuration. The information to be gained in this respect from the X-ray powder diffraction data is of necessity limited and, because of the complexity introduced by distortions in the lattice, may even be confusing. Thus, $YCrO_3$ was originally reported from the diffraction pattern of the powder to have a new type of structure (100). Looby and Katz (112) interpreted the pattern on the basis of a monoclinic distortion of the perovskite structure, but pointed out that it could be orthorhombic. Single crystals of the compound were eventually prepared by crystallization from molten lead oxide (143), and from these Geller and Wood (66) were able to show that the structure was an orthorhombic modification similar to a great many other compounds in this group. The relationship of this structure to the perovskite unit cell is shown in Figure 11.

Lanthanum cobalt oxide was first considered to have a structure represented by a rhombohedral distortion of the ideal cubic form ($a = 3.82$ A.; $\beta = 90°42'$) (6), but was later shown (210) to be isotypic with $MAlO_3$ (M = La, Pr, Nd), the detailed structure of which was determined by Geller and Bala (65) as based on a primitive rhombohedral cell ($a = 5.436$ A.; $\beta = 60°48'$).

Geller also demonstrated that the orthorhombic compounds $SmAlO_3$ and $LaGaO_3$ undergo a crystallographic transition to the rhombohedral form at 800 and 875°C., respectively, and that rhombohedral $LaAlO_3$ becomes cubic about 400°C.

The only other cubic compound in this group is $LaTiO_3$ (101), while $LaVO_3$ (102) is apparently tetragonal, but since these conclusions are based on X-ray powder diffraction data only, it is possible that the true symmetry may be orthorhombic.

Of about fifty compounds in this group, only two have the "ideal" perovskite structure, six have the rhombohedral structure, and the remainder are orthorhombic. Geller (67) has discussed the atomic coordinates. In the orthorhombic forms, the displacement of different A^{3+} cations from the ideal positions appears to decrease with increasing size of A^{3+} with the same B^{3+} cation. He concludes that it is the closeness of approach of the A^{3+} cation to the ideal position which determines the ease of transition to the rhombohedral form and not the extent of deviation from the ideal cell parameters ($a = b = c/\sqrt{2}$). The oxygen displacement from the ideal positions, while considerable in the rhombohedral structure, would be expected to decrease with rising temperatures. The oxygen atoms are also favorably disposed to change from their positions in the orthorhombic to the configurations in the rhombohedral structure. Measurements of thermal expansion of the lattices of several compounds, which is considered tantamount to increasing ionic radii, makes it clear that few transitions should be found in these compounds. The crystallographic changes should be from orthorhombic to rhombohedral and from rhombohedral to cubic, but not directly from orthorhombic to cubic. No compound has yet been found to exist in all three forms.

The precise determinations of the atomic parameters in these compounds is an important and necessary step towards the understanding of the chemical bond structure. The acquisition of data on A–O and B–O distances has led to the derivation of another set of ionic radii (68); however, it is just as empirical as other lists, inasmuch as it

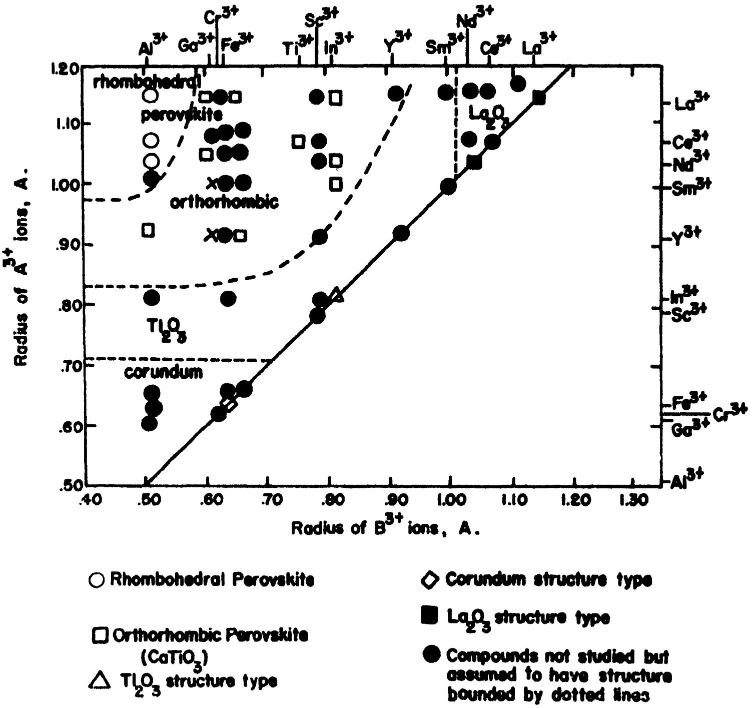


Fig. 12. Classification of $A^{3+}B^{3+}O_3$-type compounds according to cationic radii.

is based on the assumption of a specific value for the radius of the oxide ion (1.346 A.) and, indeed, that the lanthanum and the oxide ions have the same radius.

The fact that such a table of ionic radii provides some consistency to the structural variation is in itself interesting. In general, the combination of a large A^{3+} cation with the smaller B^{3+} cations suggests likelihood of the rhombohedral or cubic structure. Co^{3+} falls in this group since its radius is taken as 0.56 A., only slightly larger than that of Al^{3+} (0.558 A.). (In compounds of the $Li\,Co_{1-x}O$ type the radius of Co^{3+} is taken as 0.644 A. (90).) A classification of A^{3+}-$B^{3+}O_3$ compounds showing the relationship of structure to ionic radii has also been given by Roth (152).

Taking the radius of Co^{3+} as 0.63 A. (from Ahrens), Roth considered $LaCoO_3$ as anomalous. With Geller's value, $LaCoO_3$ falls in its proper area in the diagram shown in Figure 12. According to this classification and the radius for Ti^{3+} (0.61 A.), $LaTiO^3$ should be close to the borderline between orthorhombic and rhombohedral, while with Ahrens' value (0.76 A.) it falls clearly in the orthorhombic group.

Implicit in the search for self-consistent ionic radii is the recognition that the association of the oxide ion with four A^{3+} ions in the structure has a profound influence upon the bonding between the B^{3+} ion and oxygen. For every distinct structural type, it appears that an appropriate set of ionic radii should be sought.

The magnetic structure of lanthanum manganese oxide has drawn some interest because the introduction of Mn^{4+} into the lattice by valence compensation gives a ferromagnetic (or more probably a ferrimagnetic) material (93). $LaMnO_3$, itself, is antiferromagnetic below 100°K., and it has been shown that the ions with opposed spins lie in alternate planes (105) perpendicular to a 100 axis. With corresponding compounds of Cr^{3+} and Fe^{3+} it was found that all nearest neighbors were antiparallel, but with the Co^{3+} and Ni^{3+} compounds no magnetic ordering was observed down to 4.2°K. For the system $La(Cr_xMn_{1-x})O_3$, the magnetic structure is reported to be the same as that of $LaCrO_3$ in the range $0.40 < x < 1$, while the magnetic structure of $LaMnO_3$ is preserved only over the short range $0 < x < 0.15$ (9).

It is interesting that the range of composition over which this system is isostructural with $LaCrO_3$ is $0.33 < x < 1$ (69). $LaFe_xMn_{1-x}O_3$ has the same structure as $LaFeO_3$ at $0.5 < x \leq 1$, but with substitution of Co^{3+} for Mn^{3+} this structure is found only with $0.1 < x < 0.4$. The criterion used for structural similarity is not the inclusion in the orthorhombic group, but rather the order of the axial lengths. For the typical compound $GdFeO_3$, the order is $a < c/\sqrt{2} < b$. This order is preserved in the ranges of composition given above. In the $LaFe_xMn_{1-x}O_3$ system, when x falls below 0.5, the order of axial lengths changes to $c/\sqrt{2} < a < b$ owing to an increase in the b axis and an abnormally large decrease in c axis. These changes are unquestionably linked to the magnetic interaction between the B cations. There is also the possibility in this case that the change $Fe^{3+} + Mn^{3+} \rightarrow Fe^{2+} + Mn^{4+}$ occurs.

Vickery and Klann (203) have observed that the magnetic susceptibilities of compounds $A^{3+}MnO_3$ (A^{3+} = Pr, Nd, Dy) are greatly in excess of the additive values—rare earth ion + transition metal ion—

and appear to be greatest when both ions are capable of existing in different oxidation states. The phenomenon was more noticeable with $PrVO_3$ and $NdVO_3$, the latter giving almost double the value. It is suggested that this is due to Heisenberg exchange effects.

Many of the $A^{3+}B^{3+}O_3$ compounds appear to be essentially stoichiometric, but not many attempts to prepare nonstoichiometric phases have been recorded. Both rhombohedral and orthorhombic modifications of $LaMnO_3$ have been obtained (213), but the incidence of the rhombohedral modification seems to be dependent upon oxidation and may not represent a true crystallographic transformation. The existence of cation vacancies has been established in the system $La_{1-x}TiO_3$ (103). Homogeneous phases apparently of the cubic perovskite structure were prepared by interaction of appropriate proportions of La_2O_3, TiO_2, and Ti_2O_3 *in vacuo*. A Vegard's dependence was found over the range $0 < x < 0.3$. The high conductivities of the cation-deficient phases suggested a relationship to the tungsten bronzes, but the magnetic susceptibilities at room temperatures indicated that the electron distribution was of a different type (130). Similar phases have also been found in the system $La_{1-x}VO_3$ (102), but the range over which the tetragonal structure persists is more restricted ($0 < x \leq 0.1$). Perhaps the lanthanum–manganese system also exhibits some cation deficiencies, for the compound is often found to contain a few mole per cent Mn^{4+}, and it is not likely that excess oxygen could be harbored in the lattice interstitially.

Control of the proportions of Mn^{4+} in the crystal can be effected by charge compensation, as has been shown by Jonker and van Santen with the system $La_{1-x}Sr_x(Mn^{3+}_{1-x}Mn^{4+}_x)O_3$ (93,95).

For moderate strontium and manganese(IV) concentrations, they concluded that the magnetic saturation values could be explained on the basis of a strong positive interaction between Mn^{4+} and Mn^{3+}, and the system should be regarded as ferromagnetic. They reached a similar conclusion for the B cation interaction in the corresponding cobalt system (94) contrary to the expectations on the superexchange theory. The investigation of the electrical conductivity of these phases in a magnetic field (204) furnished additional evidence that the magnetic interaction and electron transfer are intimately connected and suggests the double exchange mechanism.

With several systems of the type $La_{1-x}A^{2+}_x(B^{3+}_{1-x}B^{4+}_x)O_3$ (where A = Ca, Sr, Ba; B = fourth period transition metal), it is found that the complete range of composition cannot be realized experimentally. Indeed, there are but few systems where x may vary from 0 to 1 without some structural change or some miscibility gap being found. One of these is $La_{1-x}Sr_x(Ti^{3+}_{1-x}Ti^{4+}_x)O_3$ (102), but with $La_{1-x}Ba_x(B^{3+}_{1-x}B^{4+}_x)O_3$, where B is iron or chromium, x cannot be made very large without introducing oxygen deficiencies. Jonker (96) has demonstrated that the substitution of Fe or Cr in the phase $La_{.85}Ba_{.15}(Mn_{1-x}B_x)O_3$ gives a sharp maximum in electrical resistivity at $x = 0.85$. The introduction of iron or chromium below this limit decreases the number of Mn^{3+} ions which can exchange with the Mn^{4+} ions. At $x = 0.85$, there are no Mn^{3+} ions, and the crystal becomes an insulator. Above $x = 0.85$, Fe^{4+} or Cr^{4+} is introduced which then exchanges with its trivalent neighbors.

Phases of the type ABO_3 with the perovskite structure where A = an alkaline earth cation and B = V, Cr, Mn, Fe, Ni apparently exist only as ion-deficient phases, except in the combination of calcium with vanadium or manganese. Anion-deficient phases such as $ABO_{2.5}$ are to be found with this structure in some cases. $SrVO_{2.5}$ apparently is of the cubic perovskite type. In view of Geller's contention about the difficulty of transition between the orthorhombic and cubic modifications of the perovskite structure, it is interesting to note that the system $La_{1-x}Sr_xVO_{3-.5x}$ shows the tetragonal structure in the range $0 \leq x < 0.6$ and the cubic structure in the range $1 > x > 0.8$. Heterogeneous products were found for intermediate values of x. No immiscibility was found, however, in the systems $LaV_{1-x}Ti_xO_3$ or in $La_{1-x}Sr_xTiO_{3-.5x}$.

B. $A^{2+}B^{4+}O_3$ COMPOUNDS

Somewhat greater flexibility in the perovskite system is obtained with higher oxidation states of the B cation. Stoichiometric compounds of the 2–4 type are found in which the A cations may be alkaline earth ions, cadmium, or lead. In addition, equimolar proportions of alkali metal cation and trivalent rare earth ions can be substituted (29). The B^{4+} cations include Ti, Zr, Hf, V, Mo, Mn, Ru, Sn, Ce, and U, but substitution of two cations with average valence of 4 is permissible. $M^{2+}_{0.5}W^{6+}_{0.5}$ (M^{2+} = Mg, Zn, Ni, or alkaline earth ion) and $M^{2+}_{1/3}M^{5+}_{2/3}$ or $M^{3+}_{1/2}M^{5+}_{1/2}$ (M^{2+} = Mg, Zn, Fe, Co, Ni, Sr, Ca; M^{3+} = Fe; M^{5+} = Nb, Ta) are examples of this kind of compensation (59,155).

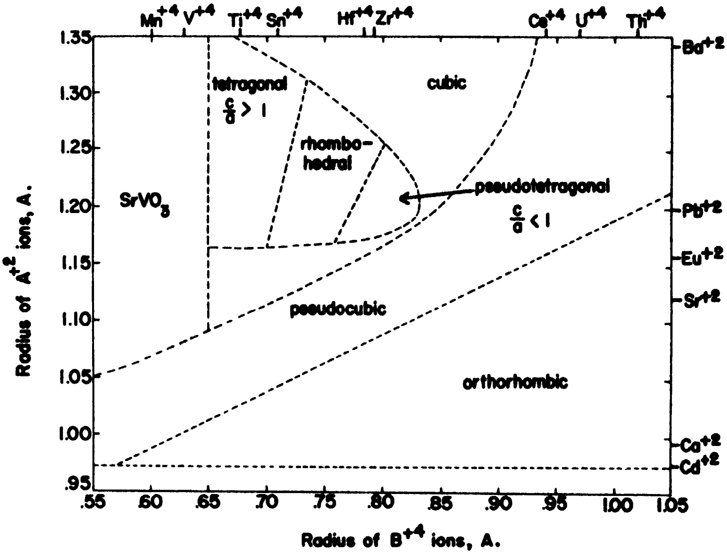


Fig. 13. Classification of $A^{2+}B^{4+}O_3$-type compounds according to cationic radii.

A number of different modifications of the perovskite structure have been recognized among phases of this kind. Following upon the original suggestions of Goldschmidt, many others have offered explanations of these distortions from the "ideal" structure on the basis of relative ionic radii. Reference to these works is given by Roth (152) who also provides a diagrammatic presentation of the data similar to that shown in Figure 13. The boundaries are determined from experimental data for room temperatures including some solid solution studies, but they have no foundation in theory.

The phases which fall in the "tetragonal" region are of special interest, since they have ferroelectric properties associated with the asymmetry of the crystal. According to the two-dimensional diagram, a substantial range of solid solutions $Ba_{1-x}Sr_xTiO_3$ should have this structure. The experimental fact is that a very small amount of strontium causes the adoption of the cubic structure. To explain phenomena of this kind, Roth suggests the inclusion of another parameter, the polarizability of the A cation.

A two-dimensional plot of this function at the B cation radius corresponding to Ti^{4+} is shown in Figure 14. Such a scheme is admit-

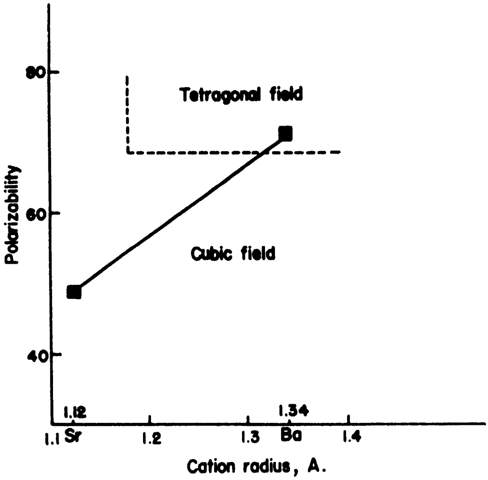


Fig. 14. The effect of A-cation polarizability on deformation of the perovskite structure.

tedly a very rough approximation, since the polarizabilities of the B cations are neglected, simply from lack of information. It is quite apparent that the influence of the A cation upon the oxide ion has a very important bearing on the bonding of the oxide ion to the B cation. Roth's treatment seems to be the reciprocal approach. More fundamental interpretation will probably have to await the precise determination of atomic parameters, and these are accurately known for relatively few of the systems in this group. Meanwhile the approximate classification such as that of Figure 13 provides a useful guide to practical synthesis. The structural map of Figure 13 would be subject to a substantial modification at different temperatures. Barium titanium oxide, for example, has the following transformations:

$$\text{Rhombohedral} \xrightleftharpoons{-100^\circ\text{C.}} \text{orthorhombic} \xrightleftharpoons{0^\circ\text{C.}} \text{tetragonal} \xrightleftharpoons{120^\circ\text{C.}} \text{cubic}$$

while lead titanium oxide appears to have only one transition

$$\text{Tetragonal} \xrightleftharpoons{490^\circ} \text{cubic}$$

Since these compounds and their solid solutions are the only examples of the tetragonal ($c/a > 1$) phases, this region would be absent from structure diagrams for temperatures above 500°C.

The great interest shown in barium titanium oxide centers on the outstanding ferroelectric properties of the tetragonal form in which the titanium ion is slightly displaced along the *c* axis. Since these displacements occur in the same direction, a spontaneous polarization of the crystal results (for a discussion of the ferroelectric properties of barium titanate, see refs. 104,129; for summary of crystallographic transitions, see ref. 179). The tetragonal crystals, such as $PbZrO_3$, in which $c/a < 1$ are antiferroelectric, the ionic displacements occurring in such a manner as to compensate each other. Neutron diffraction patterns of tetragonal $BaTiO_3$ and $PbTiO_3$ show that the oxide ion is also displaced from its "ideal" position and that the displacement of the ions is much larger in the case of the lead compound (164).

Hopes of turning up materials with improved ferroelectric properties have led to numerous investigations of solid solutions of known substances with perovskite-like structures. There is, consequently, a large body of information concerning the effect of cationic substitution upon crystal structure and temperatures of phase transitions, which should be useful in arriving at a more detailed theory of the chemical bonding in systems of this kind.

The question which should be answered is why some compounds are not found with this type of structure when the ionic radii are suitable. The existence of the compound $PbSnO_3$ ($t = 0.87$) with a perovskite-like structure is doubtful according to Roth (152), but $Pb(Ti_{1-x}Sn_x)O_3$ has the tetragonal perovskite structure over the range $0 < x < 0.53$ and the rhombohedral structure when $.55 < x < .75$, but heterogenous products are found above this last value (199). On the other hand, $PbTiO_3$–$BaSnO_3$ forms solid solutions over the entire range of composition (198).

The existence of a perovskite-type compound in which both A and B cations are post-transition metals has not been confirmed, and it might be suggested that the influence of directive bond formation becomes dominant in determining the atomic arrangement with high concentration of ions of this type.

The system $Sr(Ru_{1-x}Ir_x)O_3$ (140) yields a perovskite-type phase over the range $0 < x \leq 0.5$. With higher proportions of iridium, the phase Sr_2RuO_4 appears, yet the radii of Ru^{4+} and Ir^{4+} do not differ by more than 2%. There are other instances of this difference in behavior of transition elements of the fifth and sixth periods.

$MMoO_3$ (where M = Ca, Sr, Ba) phases with the perovskite-type structure are readily formed by heating MoO_2 and the alkaline earth oxide *in vacuo* (159,160), but no corresponding phases containing tungsten have been obtained.

Several nonstoichiometric phases have been found in this group of compounds. Cation-deficient crystals are less common than the oxygen-deficient type. They are usually prepared by heating *in vacuo* mixtures which should give the transition metal the desired oxidation state if a homogeneous product is formed. Thus $SrMO_{3-x}$ ($M =$ Ti, V) may be formed from the mixtures $SrO + (1 - x)\ MO_2 + {}^1/_2x\ M_2O_3$ and $SrO + (1 - x)\ MO_2 + x\ M$ (102).

In these cases, the value of x for the titanium system ranges from 0 to $^1/_2$, but for the vanadium system, from 0 to 0.25, the structure and lattice constant remaining essentially the same over the entire range. Cation-deficient phases were made in the same way using mixtures of composition $(0.5 + x)\ SrO + 2x\ NbO_2 + (0.5 - x)\ Nb_2O_5$ to give, presumably, $Sr_{0.5+x}Nb^{4+}_{2x}Nb^{5+}_{1-2x}O_3$. Over the range $0.2 < x \leq 0.45$ (145) a homogeneous phase was formed in which the structure was the cubic perovskite type, and the lattice constant increased with increasing strontium content. Similar techniques applied to corresponding compositions of molybdenum have failed to yield evidence of cation deficiency. Tantalum gives cation-deficient phases, but of quite different structure (60).

In several cases, anion-deficient phases are formed merely by heating the alkaline earth oxide and the transition metal oxide in air. With some of these, $SrFeO_{3-x}$ (27,96,213), $CaMnO_{3-x}$ (93,213), $SrCoO_{3-x}$ (213), the range of homogeneity may be somewhat restricted.

No conclusive evidence has yet been found for the ordering of the oxygen vacancies, although such an interpretation has been offered for the structure of $BaFeO_{2.62}$ (49), but there is reason to believe that several structures may be formed with the system $BaFeO_{3-x}$ depending on the many variable factors inherent in all of the methods of preparation. This situation prevails in the mixed oxides of the alkaline earths with the oxides of iron, cobalt (177), and nickel (107–109), where no higher oxides are available for controlled preparations.

The stoichiometric compound $BaNiO_3$ was obtained below 700°C. by Lander and Wooten, and the structure described as related to the perovskite structure in that it contains close-packed layers of composition BaO_3, but these layers are stacked in hexagonal close packing.

The nickel atoms are in the octahedral cavities formed by the oxide ions. The result of such an arrangement is, however, to produce strings of NiO_6 octahedra parallel to the *c* axis of the hexagonal crystals. These octahedra share opposite faces, and the nickel atoms are brought together close enough to suggest the formation of metal–metal bonding. With rising temperatures, loss of oxygen occurred giving rise to different but unknown structures, but at composition $BaNiO_2$ the nickel appeared to assume a square configuration with oxygen. Gushee (80) found, however, that the hexagonal structure was obtained at 680°C. with composition $BaNiO_{2.5}$ and that $BaCoO_{2.85}$ had a similar structure. The data suggest that a range of homogeneity exists from $BaNiO_3$ to $BaNiO_{2.5}$ below 700°C., and that at higher temperatures another crystallographic modification of composition $BaNiO_{2.5}$ is formed. The stoichiometric phase $BaCoO_3$ has not been obtained.

It is difficult to evaluate the significance of vacancies or the presence of impurities in determining crystal structure. Remeika (144) has shown that single crystals of barium titanate are readily grown from a potassium fluoride flux containing a small amount of iron. Crystals containing about 0.2% iron had a substantially lower Curie temperature than pure barium titanate. Those prepared from 30% TiO_2 + 2.5% Fe_2O_3 + 67.5% KF were cubic at room temperatures.

At high temperatures, contamination of crystals by contact with containers is difficult to avoid, and small losses of oxygen are not readily detected. Consequently, the transformation of cubic barium titanate to a hexagonal form which occurs above 1400°C. should be regarded with some reservation. Rase and Roy (142) have observed that the presence of barium chloride raises this transition temperature above 1500°C. Matthias (124) has grown single crystals of hexagonal barium titanate by cooling a molten mixture of barium chloride, barium carbonate, and titanium dioxide from 1200°C. When grown from a flux of potassium and sodium carbonate in a platinum crucible, the crystals were deep amber colored (15). It was from such crystals that the hexagonal structure was determined (31). In common with the perovskite structure, it consists of layers of composition BaO_3 in a close-packed arrangement with the sequence of layers ABCACB. The titanium ions are in octahedral coordination with oxygen between the layers, and two-thirds of the TiO_6 octahedra oc-

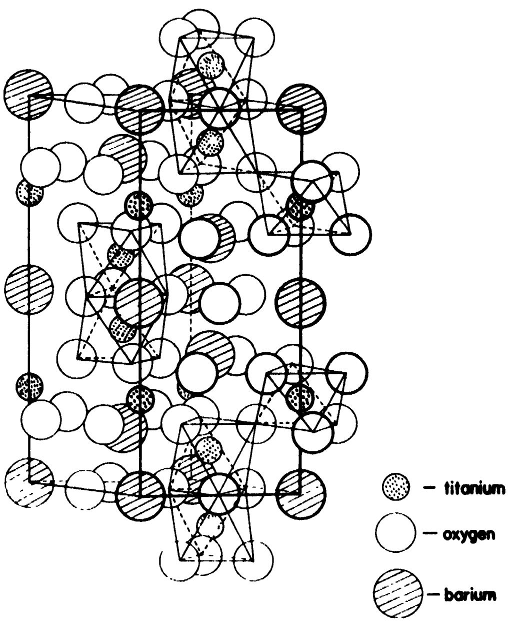


Fig. 15. The structure of hexagonal barium titanate, $BaTiO_3$.

cur in pairs which share a face. The structure is shown in Figure 15. It may be regarded as intermediate between the cubic perovskite and the $BaNiO_3$ structure.

Similar structures have been found with phases which definitely contain platinum metals, such as $Ba(Pt_{.25}Ti_{.75})O_3$ (16) and $Ba(Ti_{1-x}Ir_x)O_3$ where $0.15 < x \leq 0.5$ (Dickinson, unpublished data). A closely related structure is suggested for a barium iron oxide $BaFeO_{3-x}$ (123), the probable value of x being about 0.26 (80).

A distinction may be drawn between the nonstoichiometric and the ion-deficient phases in which the vacancies are ordered by regarding the latter as new phases and the nonstoichiometric as containing of necessity random vacancies. Annealing under suitable conditions should favor the ordering process, but these conditions have not been found for the phases described here.

Ordered arrangements of cations are found in compounds such as $A^{2+}(M^{2+}_{0.5}W^{6+}_{0.5})O_3$ and $A^{2+}(M^{2+}_{1/3}Ta^{5+}_{2/3})O_3$. In the former with A^{2+} = Sr or Ba, M^{2+} may be small cations such as nickel, zinc, or magne-

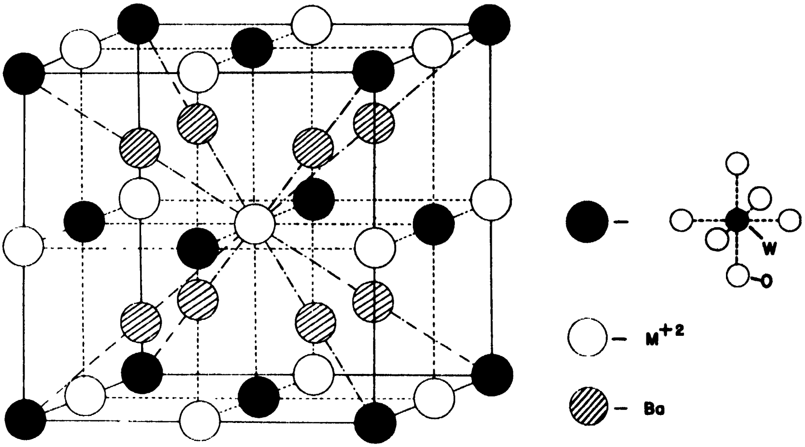


Fig. 16. The structure of Ba_3WO_6 showing its relationship to the perovskite structure.

sium (57), but Steward and Rooksby (173) have shown the M^{2+} may also be an alkaline earth metal. The compound $Ba(Ca_{0.5}W_{0.5})O_3$ has a face-centered cubic structure (a = 8.39 A.) (178) in which the unit cell consists of eight perovskite units as shown in Figure 16. The calcium and tungsten ions which occupy the B position are ordered with the tungsten at the cube corners and face-centered positions and the calcium ions at the middle of the edges and at the center of the large cube. A similar arrangement is proposed for $Ba(Ba_{0.5}W_{0.5})O_3$. This can be regarded as Ba_3WO_6 in which the WO_6 ion is isolated in the crystal and one-third of the barium ions are in octahedral coordination, the remaining two-thirds in twelve-fold coordination.

The tantalum system is apparently rather similar, except that the different ratio of M^{2+} to Ta^{5+} calls for a larger unit cell consisting of nine perovskite units (61). The atomic parameters have not been determined.

Analogous to $Ba(Ca_{0.5}W_{0.5})O_3$ are the compounds $M^{2+}La_{0.5}Ta_{0.5}O_3$ and $Sr(Sr_{0.5}Ta_{0.5})O_{2.75}$, the latter containing anion vacancies (28). The structure of the compound $Ba(Ba_{0.5}Ta_{0.5})O_{2.75}$ has been confirmed by single crystal X-ray diffraction studies (61). No evidence for ordering of the anion vacancies has been found.

The structure of compounds of this type is similar to that of

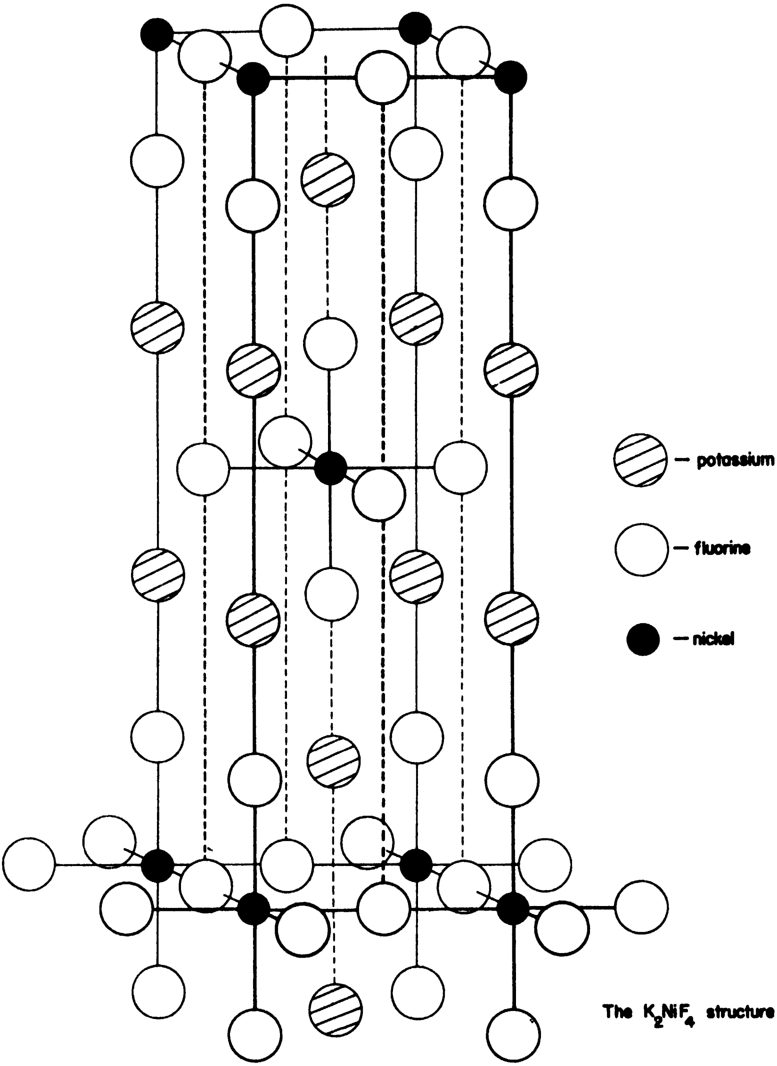


Fig. 17. The K_2NiF_4 structure.

$(NH_4)_3FeF_6$ (134). Another complex fluoride which provides a structure type for mixed oxides is K_2NiF_4, which Baltz and Plieth (7) suggested as the prototype for Sr_2TiO_4. Other oxides which have been

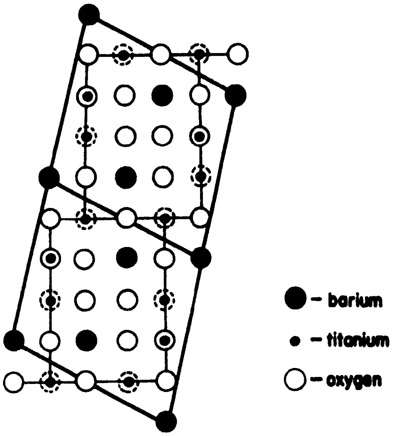


Fig. 18. The structure of $Ba_6Ti_{12}O_{30}$.

shown to adopt this structure are Sr_2IrO_4 (141), Ca_2MnO_4 and $SrLaAlO_4$ (156), La_2NiO_4 (138), and Sr_2RuO_4 and Sr_2RhO_4 (140).

The atomic arrangement shown in Figure 17 is similar to that found in the perovskite structure and may be described as a layer lattice in which layers consisting of BO_6 octahedra joined through the equatorial oxygens are separated by layers of perovskite structure. The A cation is in nine-fold coordination with oxygen. The layers are normal to the *c* axis which is about three times the length of the normal perovskite unit. The geometry of the crystal suggests the same dependence on relative ionic radii as is expressed in the Goldschmidt relationship for the perovskite structure, but it appears that the tolerance factor is more critical in this case. The work of Rabenau and Eckerlin (138) suggests that the lower limit of tolerance factor for the tetragonal structure is represented in $LaSmNiO_4$ (211). The compounds La_2CoO_4 and Nd_2NiO_4 appear to have a related orthorhombic structure. A corresponding samarium nickel oxide could not be prepared. Scholder (161) has reported the preparation of compounds A_2BO_4 (where A = Ba, Sr; B = Ti, Cr, Mn, Fe, Co), but the details of the structures are not known.

Many other phases may be obtained by heating mixtures containing AO and BO_2 oxides in different proportions. In most of these, the B cation is in octahedral coordination with oxygen. The $BaO \cdot 2\ TiO_2$ structure (84) contains chains of TiO_6 octahedra running parallel to the short B axis of the monoclinic cell. These chains are connected by corner and edge sharing of the oxygen octahedra forming large tunnels in which the barium atoms lie in twelve-fold coordination with oxygen. A schematic representation of this is shown in Figure 18. A similar structure has been suggested for BaO.4 TiO_2 (192), but one would imagine that more cross-linking among the TiO_6 octahedra would be necessary with this composition.

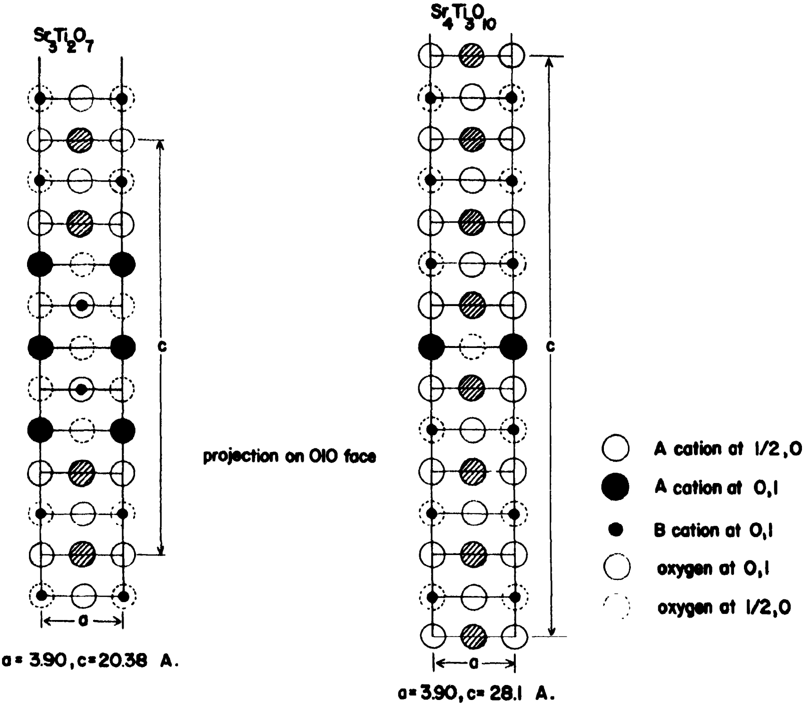


Fig. 19. The layer-type structures of $Sr_3Ti_2O_7$ and $Sr_4Ti_3O_{10}$.

The structures of the compounds $Sr_4Ti_3O_{10}$ and $Sr_3Ti_2O_7$ as determined by Ruddlesden and Popper (157) are illustrated in Figure 19. They represent the connecting links between $SrTiO_3$ and Sr_2TiO_4. If X represents the layer of composition TiO_2 and Y the layer of SrO normal to the c axis, the succession of these layers may be represented as:

$SrTiO_3$	$XY, XY, \ldots$
$Sr_4Ti_3O_{10}$	$XY, XY, XY, Y, XY, XY, XY, Y, \ldots$
$Sr_3Ti_2O_7$	$XY, XY, Y, XY, Y, \ldots$
Sr_2TiO_4	$XY, Y, XY, Y, \ldots$

Longer successions of XY (perovskite layers) were not found. These compounds in the perovskite system offer an interesting analogy with the magnetoplumbite type in the spinel system.

A large excess of alkaline earth oxide in the reaction mixtures may lead to a structure which is typical for some A_4BX_6 compounds. Examples of this are Sr_4BO_6, where B = Rh, Ir, Pt (140). The platinum metals are in octahedral coordination with oxygen. These octahedra are connected through strontium ions in chains running parallel to the *c* axis of the hexagonal crystals, the connecting strontium ions being in a trigonal prism arrangement of the oxygen ions forming the faces of two adjacent BO_6 octahedra. The other strontium ions lie between the chains in an irregular eight-fold coordination with oxygen. The structure is the same as that of K_4CdCl_6 (10).

Barium and calcium compounds of this type have not been prepared, and it seems that barium does not readily occur in phases with K_2NiF_4 structure. This might be attributable to the differences in ionic radii, yet in the structure proposed by Rooksby for Ba_3WO_6 one-third of the barium ions are in six-fold coordination.

Just as the 3–3 perovskites and the garnets are alternative structures, so it would seem that with the 2–4 compounds a silicate structure is also an alternative. Ba_2TiO_4 (149), reported to be isotypic with Ba_2SiO_4, has titanium in an unusual tetrahedral coordination. It is interesting to note that although Sr_2SiO_4 and Ba_2SiO_4 form a complete series of solid solutions, Sr_2TiO_4 has not been obtained with the silicate type of structure. The systematic morphology of these different structures has not yet been worked out.

The type of disorder involving some randomness in the distribution of cations over A and B sites, which is so common among the compounds with the spinel structure, does not seem to occur to an appreciable extent in the perovskite-like compounds. It would not be expected, since the ionic radii of the A and B cations are so different, but the similarity in structure of the A_3BO_6 compounds suggests that such disorder would be possible geometrically. In this case, however, the excess A cation is substituted in B sites. The only instance in which a B cation is assumed to occupy A sites is the compound SrV_2O_4, which has been assigned a perovskite structure with the formula $(Sr_{0.67}V_{0.33})VO_{2.67}$ (158). One-third of the A sites are occupied by vanadium(III), and there are oxygen vacancies. Attempts to repeat this work have not been successful.

While small A cations with B cations from the fourth period transition elements tend to form mixed oxides of the ilmenite type, the transition metals of the later periods do not seem to give this structure. The platinum metals do not give mixed oxides with magnesium oxide under the usual conditions of solid phase reactions. Molybdenum dioxide gives compounds of the type $M^{2+}Mo_3O_8$, where M^{2+} = Mg, Zn, Cd, Fe, Co, Ni (125). The Mo^{4+} ions appear in this structure in triangular groups in which the short distance between the atoms suggests metal–metal bonding. The magnesium and zinc compounds are diamagnetic. The M^{2+} cations occupy equal numbers of tetrahedral and octahedral sites, and the paramagnetism of the iron and cobalt compounds at room temperatures indicates four and three unpaired electrons, respectively. No corresponding compounds of tungsten or rhenium could be prepared, but the mineral nolanite, a vanadium iron oxide containing both V^{3+} and V^{4+}, has been found to have a similar structure (83).

C. $A^+B^{5+}O_3$ COMPOUNDS

Interest in the 1–5 perovskites has focused mainly upon the ferroelectric properties and attempts to correlate these with crystallographic transitions. $KNbO_3$, which is strongly ferroelectric, shows a sudden linear distortion at the Curie temperature (165), and $NaNbO_3$, which is antiferroelectric, has a maximum in the permittivity-temperature curve near the temperature at which the orthorhombic to tetragonal transition occurs (165). Similar effects have been observed with $AgNbO_3$ which undergoes the same series of crystallographic changes as $NaNbO_3$, namely, orthorhombic → tetragonal → cubic (56). Other maxima in the permittivity-temperature curve of $AgNbO_3$, however, could not be associated with any crystallographic discontinuities, and for $AgTa_{0.5}Nb_{0.5}O_3$ no correlation among these properties was found.

In the cubic perovskite structure, the Nb—O—Nb linkages form linear chains, while in the tetragonal and orthorhombic modifications the chains are puckered. Francombe attributes this to ionic radii effects and, taking $R_{Nb} = R_{Ta} = 0.68$ A. with $R_O = 1.32$ A., assumes that linear chains would be possible when the perovskite cell edge becomes 4.00 A. The cell dimensions at which $AgNbO_3$ and $AgTaO_3$ become cubic are 3.95 and 3.96 A., respectively. This "puckering" transition temperature occurs at 3.94 A. for solid solutions of $NaNbO_3$ with $KNbO_3$, $Cd_{0.5}NbO_3$, and $Pb_{0.5}NbO_3$.

Pentavalent B cations in the perovskite structure seem to promote the capacity for A cation deficiencies. The stoichiometric compound $PbNb_2O_6$ has been shown to exist in a form which can be described as a rhombohedral modification of the perovskite structure (55) similar to the rhombohedral $A^{3+}B^{3+}O_3$ compounds.

The rhombohedral cell is derived from a rhombohedrally distorted cell consisting of eight unit perovskite cells in which alternate A cation sites are vacant. This form of $PbNb_2O_6$ is prepared at 1200°C. and is not ferroelectric, but at 1350°C. a ferroelectric modification with an orthorhombic structure is formed. The lattice parameters (a = 17.51 A.; b = 17.81 A.; c = 7.73 A.), suggest that some longer range order is adopted, and that the structure may be derived from a large monoclinic cell consisting of six perovskite units in the *ab* plane and two in the *c* direction. Roth (153) has observed that the orthorhombic form transforms irreversibly to the rhombohedral form at 700°C. The Curie temperature is about 570°C. The fact that the change is not reversible suggests that the transformation to the orthorhombic form is not due to a "puckering" phenomenon but is related to a different ordering of the A cations.

In the system $Na_{1-2x}Cd_xNbO_3$ the perovskite type structure is formed only for small values of x (110). When x becomes larger, $CdNb_2O_6$ or the pyrochlorite phase, $Cd_2Nb_2O_7$, is formed as a separate phase. This suggests that random vacancies are not readily formed with systems of this kind.

Some interesting phases with the perovskite-type structure are formed with univalent A cations and tungsten. These are commonly called tungsten bronzes because of the metallic appearance of some of the phases in the system Na_xWO_3. In the range $0.3 < x < 0.95$, the structure is the cubic perovskite type. A tetragonal form which is probably related to the perovskite structure exists in the range $0.1 < x < 0.28$, and below this value a monoclinic structure is found (114,115).

The monoclinic WO_3, itself, may be said to be related to the perovskite structure, inasmuch as it consists of WO_6 octahedra sharing corners (5). The existence of these phases and the linear increase in lattice constant of the cubic phase with increasing sodium content suggests that we are dealing with a three-dimensional framework of W–O–W bonds in which the large cavities may be progressively filled with sodium ions. No evidence has been obtained that ordering of the cations occurs at any concentration (172).

Most of these phases have high electronic conductivity (30,174). Brown and Banks showed that the resistivity of the cubic sodium tungsten bronzes decreased linearly with decreasing temperature from 360 to −160°C., and that a minimum in resistance occurred at the composition $Na_{0.7}WO_3$. The mobility of the electrons at this composition is about 35% of their mobility in metallic sodium. The Hall coefficient was found to correspond to one free electron per sodium atom in the crystal from $0.584 < x < 0.97$ (62). The magnetic susceptibilities of the cubic sodium tungsten bronzes are comparable to those of metals (106). All of these properties suggest that the sodium atoms are dispersed in the lattice of the tungsten trioxide and ionized to Na^+ and free electrons. An interesting observation which strongly supports the idea of a framework structure is that a sharp decrease in the coefficient of thermal expansion of the cubic tungsten bronzes occurs at temperatures ranging from 165 to 250°C., and that tungsten trioxide itself also shows a marked decrease in expansion rate along the *b* axis at about 300°C. (150). The low resistivity of these phases, which is of the order of 10^{-5} ohm-cm., and the high activation energy for the diffusion of sodium in the lattice ($\Delta H = 51.8$ kcal./mole) (172) account satisfactorily for the absence of appreciable ordering of the cations and vacancies in the system. There appears to be very little electron trapping such as would be suggested by the notation $Na_{0.7}(W^{5+}_{0.7}W^{6+}_{0.3})O_3$. Furthermore, the stoichiometric compound $NaWO_3$ apparently does not exist, and this does not seem to be due to the overcrowding of the lattice with large sodium ions, for in the corresponding lithium phases, Li_xWO_3, the upper limit of x is probably less than 0.5(116,175), and the lithium ions are randomly distributed over the A sites. Some evidence for cationic conductivity has been found in the lithium system (175). Somewhat analogous phases Cu_xWO_3 have also been prepared (38) with $x = 0.6$, orthorhombic crystals ($a = 3.88$ A.; $b = 3.73$ A.; $c = 7.74$ A.) are obtained which may be structurally related to monoclinic WO_3 ($a = 7.285$ A.; $b = 7.517$ A.; $c = 3.835$ A.; $\beta = 90.9°$). The structure becomes triclinic at $x = 0.77$. These are semiconductors but with quite low resistivities of the order of 10 ohm-cm.

The occupancy of A sites in perovskite-like crystals by small cations such as lithium and copper is difficult to explain on the basis of ionic packing. The concept of an expandable framework structure formed by linked WO_6 octahedra is more attractive, but, in addition, the property of high conductivity appears to be required for large ranges of nonstoichiometry.

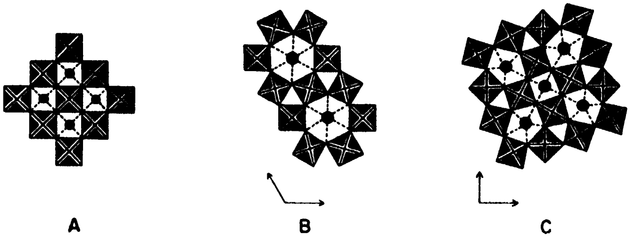


Fig. 20. Framework structures formed by BO_6 octahedra-sharing corners. A: The perovskite-type structure formed by the addition of metal atoms (black circles) to the cubic interstitial sites. B: "Tunnels" of octahedra forming the hexagonal tungsten bronzes seen in projection. The circles represent the 12-coordinated atoms Cs, Rb, or K. C: Tetragonal tungsten bronze structure in projection. The K atoms (circles) are 10-coordinated in tunnels and 8-coordinated in residual "cages" of the cubic bronze type at the center.

The preparation of tungsten bronzes is easily accomplished by electrolytic or chemical reduction of molten mixtures of alkali tungstates and tungsten trioxide. Molybdenum does not yield similar phases (176), although some have been reported, but some molybdenum may be introduced to give crystalline substances of approximate composition $Na_{0.25}W_{1-x}Mo_xO_3$ $(0 \leq x < 0.1)$. These crystals are insulators at room temperature (126).

With large alkali metal cations tungsten yields compounds which may be described in terms of corner-linked WO_6 octahedra joined in such a way as to provide larger cavities than those available in the perovskite structure. K_xWO_3 $(0.475 < x < 0.57)$ has a tetragonal structure and M_xWO_3 (M = K, Rb, Cs) $(0.27 < x < 0.32)$ a hexagonal structure (114,117). The structure of the tetragonal potassium compound suggests a maximum of $x = 0.6$ (118), while the hexagonal structure permits a maximum of $x = {}^1/_3$.

From the similarity in diffraction patterns, Magneli suggests that in the tetragonal sodium and potassium tungsten oxides the arrangement of the WO_6 octahedra is essentially the same.

In a general review of nonstoichiometric compounds, Wadsley (206) refers to these phases as "tunnel" compounds. The large cavities occupied by the alkali metals can be regarded as being formed by rings of WO_6 octahedra sharing equatorial oxygens. These rings lie normal to the *c* axis of the crystal and form tunnels along the axis as illustrated in Figure 20. In the tetragonal structure four- and five-membered rings, and in the hexagonal structure six-membered rings, may be occupied.

VII. Mixed Oxides of the MO_2 Type

Typical structures of these compounds may be considered in order of decreasing coordination numbers of the cations. The larger cations (0.8 A. radius or greater) tend to adopt the fluorite (CaF_2) structure with the cations in eight-fold coordination with oxygen. The ions with radius suitable for six-fold coordination frequently give the rutile-type structure. Combinations of larger and smaller cations occur in a variety of structures of which zircon, $ZrSiO_4$, and schleelite, $CaWO_4$, are examples.

A. MIXED OXIDES OF THE FLUORITE TYPE

Zirconium and hafnium are the only transition metals which have dioxides with structures related to that of fluorite. The lanthanide elements which can be oxidized to the tetravalent state (Ce, Pr, Tb) and the actinide elements from thorium to americium inclusive all give dioxides of this type (98).

Zirconium dioxide is monoclinic at room temperatures but transforms to a tetragonal structure at high temperatures. This inversion prohibits the use of sintered zirconia as a refractory material. The presence of varying amounts of other cations, however, stabilizes the fluorite structure (43,154).

A unique phase, $M_2^{3+}Zr_2O_7$, is formed with large trivalent cations such as La^{3+} (190) and Ce^{3+} (33). The cerium compound was formed by the reaction of $BaZrO_3$ with Ce^{3+} in fused barium chloride *in vacuo*. The structure of $M_2Zr_2O_7$ appears to be related to the fluorite structure, the edge of the cubic cell being taken as twice that of the fluorite cell because of the presence of some weak lines in the X-ray powder diffraction pattern. Upon heating in air at 1000°C., $Ce_2Zr_2O_7$ yields $CeZrO_4$ with the simple fluorite structure. This suggests that the large unit cell of $M_2^{3+}Zr_2O_7$ is required because of ordered anion vacancies and that the cations are randomly distributed. It is strange that solid solutions of CeO_2 and ZrO_2 prepared at 2000°C. are unstable with less than 90 mole % CeO_2 (47).

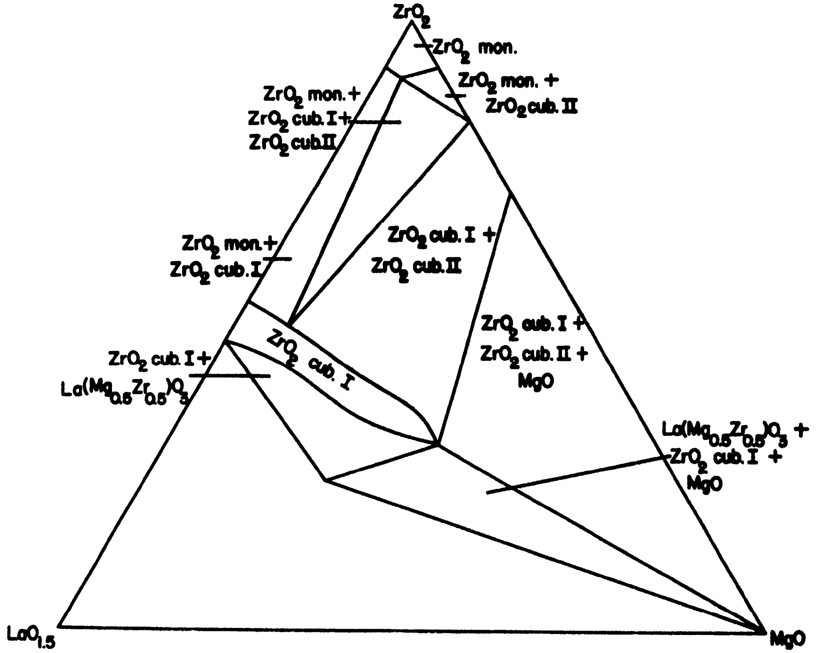

ZrO2
ZrO2 mon.
ZrO2 mon. + ZrO2 cub. II
ZrO2 mon. + ZrO2 cub. I + ZrO2 cub. II
ZrO2 mon. + ZrO2 cub. I
ZrO2 cub. I + ZrO2 cub. II
ZrO2 cub. I + La(Mg0.5Zr0.5)O3
ZrO2 cub. I
ZrO2 cub. I + ZrO2 cub. II + MgO
La(Mg0.5Zr0.5)O3 + ZrO2 cub. I + MgO
LaO1.5
MgO

Fig. 21. The phase diagram of the systems ZrO_2–$LaO_{8.5}$–MgO.

From X-ray powder diffraction data it is difficult to distinguish between a defect fluorite structure and the pyrochlorite structure which is adopted by $Cd_2Nb_2O_7$. In the latter, the cadmium ions are in eight-fold and the niobium in octahedral coordination with oxygen. Jona, Shirane, and Pepinsky (91) have discussed the relationship of this structure to both the perovskite and fluorite structures.

Ternary phase diagrams by Rabenau of systems La_2O_3–ZrO_2–MO (M = Ca or Mg) indicate that the fluorite-like phases formed with small amounts of MgO and CaO are not miscible with those formed by small amounts of La_2O_3 (139). Phases with the perovskite structure $La(M_{0.5}Zr_{0.5})O_3$ as well as the phases $La_2Zr_2O_7$ were obtained.

The phase diagram for the magnesium system is shown in Figure 21. $La_2Zr_2O_7$ forms a continuous phase with magnesium oxide up to about 40 mole % without appreciable change in lattice constant. Upon the assumption that the lanthanum and zirconium are equally displaced by magnesium from the cation lattice sites, and from consideration of the density variation with increasing proportions of magnesium oxide, Rabenau concludes that at the solubility limit (50 mole % MgO) the composition of the fluorite unit cell should be represented as $La_{4/3}Zr_{4/3}Mg_{4/3}(Mg_{4/3})O_{22/3}\square_{2/3}$. Half of the magnesium is assumed to enter interstitial positions; the cation sites are randomly and equally occupied by Mg^{2+}, La^{3+}, and Zr^{4+} ions; and there is an average of $^2/_3$ anion vacancy per unit cell. The solubility of calcium oxide in $La_2Zr_2O_7$ is negligible.

While the substitution of divalent and trivalent cations in the ZrO_2 lattice leads to the formation of a cubic phase at about 10–15 mole % of the substituent, the substitution of tetravalent uranium in this range leads to a face-centered tetragonal phase (212) characteristic of the high temperature form of pure ZrO_2. The tetragonal phase persists in samples quenched from 2300°C. up to about 45 mole % uranium, the *a* and *c* axes gradually approaching the same value with increasing proportions of uranium. At higher concentrations of uranium, the structure is cubic. A continuous solid solution is obtained above 1950°C.

It is of some interest to note that the cubic fluorite phase is stabilized more readily by creating anion deficiencies than it is by substitution of a larger cation. The weighted average of the radii of Zr^{4+} and U^{4+} at 45 mole % uranium is about 0.95 A., using the Goldschmidt radii. For contact of all ions in the fluorite structure, the cation radius should be about 0.96 A. on this scale. The distortion to the tetragonal form could be attributed to an adjustment of the oxygen parameters when the cation becomes too small.

Two series of mixed oxides having the general formula $A_K^{Z+}B_{4-K}^{4+}O_{8-K/2(4-Z)}$ are said to occur with the fluorite-type lattice (162); when B = Ti, A may be Fe, Co, Ni and when B = Zr, A may be V, Cr, Mo, W, Mn. The composition of these phases was not determined but was thought to be in the range $^1/_3 \leq A/B < 1$. The oxidation state (Z) of the A cation was not specified. The inclusion of the titanium series in this class could bear re-examination.

The systems Ce_2O_3–CeO_2 (14), Pr_2O_3–PrO_2 (51,79,82,168), and Tb_2O_3–TbO_2 (79,81,169) all show intermediate phases which may be regarded as mixed metal oxides. These phases are probably to be regarded as defect fluorite phases with ordered anion vacancies, since the cubic lattice constants derived from the strong lines of the X-ray powder diffraction patterns have been shown to have a linear dependence on composition between the limits M_2O_3 and MO_2 (98). It is typical of these systems that the lattice constant decreases with increasing oxygen content. Any expansion of the lattice which would be brought about by the introduction of an oxide ion into a vacant anion site is more than compensated by the decrease in the size of the oxidized cation or by an increase in polarization due to the higher charge on the cation.

By reduction of CeO_2 with hydrogen at high temperatures and annealing the products at temperatures near 1000°C. *in vacuo*, Bevan (14) has shown that no less than five different phases exist in the composition range from CeO_2 to Ce_2O_3.

TABLE III

Changes in Structure of Binary Rare Earth Oxides with Changing Composition

Structure type	x in		
	CeO_x	PrO_x	TbO_x
Fluorite	2.0	2.0–1.74	2.0–1.801
Rhombohedral	1.812–1.775	1.717–1.714	1.76–1.66
Rhombohedral	1.722–1.717		
C rare earth	1.688–1.651	1.703–1.700	1.54–1.500
A rare earth	1.53–1.50	1.640–1.5	

The praeseodymium and terbium systems (81,82) give apparently similar phases. These are compared in Table III. The similarities are obvious, but not much emphasis can be placed on the differences since the systems were studied by quite different techniques. It should be noted that the compositions Pr_6O_{11} and Tb_4O_7, which are usually obtained by ignition in air, both occur in phases which have a considerable range of homogeneity, the former in the defect structure range, the latter in the rhombohedral range.

Mixed oxides containing trivalent and tetravalent rare earth elements have been prepared by heating intimate mixtures of the oxides in oxygen at high pressures (127). A continuous change from the fluorite structure to the C rare earth structure was observed in the systems Y^{3+}–Ce^{4+}, Y^{3+}–Pr^{4+}, Gd^{3+}–Ce^{4+}, and Sm^{3+}–Ce^{4+} but was not in evidence with Pr^{3+}–Ce^{4+}. The appearance of the X-ray reflections characteristic of the C rare earth structure was noticed in the yttrium systems at about 15 mole % yttrium, in the gadolinium and samarium systems at progressively greater concentrations of the trivalent element. The ordering of the vacant anion sites appears to be favored by the smaller trivalent ions.

The mixed oxide systems containing different elements in contrast to those containing the same element in two oxidation states do not readily produce intermediate phases. Bevan (14) attributes this to the low mobility of the cation in the fluorite-type lattice. With the same element in two different oxidation states, the cations can assume an ordered arrangement by electron transfer. Hence, one may assume that the rhombohedral distortions are due to an ordered arrangement of the +4 and +3 cations.

Although the defect fluorite structure appears to be a common one among compounds of the type $A_2B_2O_7$ (where A = a lanthanon element and B = a lanthanon or a tetravalent transition element of the fifth or sixth period), the electrical properties do not appear to have been studied extensively. The resistivity composition curve of the fluorite-type phase in the CaO–ZrO_2 system at 1000°C. has a minimum of 250 ohm-cm. at 13 mole % CaO, which is the composition at which the fluorite phase becomes stable and a maximum of 100,000 ohm-cm. at $CaO{\cdot}2\ ZrO_2$ (191).

Cation deficiency, which might occur in oxides of the fluorite type containing an oxidizable cation, has not been established. Protoactinium, uranium, neptunium, and plutonium are the elements which provide this possibility. The fluorite-type phase UO_{2+x} has been recorded over the range $-0.25 < x < +0.25$ (98), although it is likely that toward these limits the phase may be metastable. In the range $0 < x < 0.2$, there appears to be no appreciable change in lattice constant, but annealing of samples of composition $UO_{2.2}$ above 250°C. yields two phases (3). A face-centered tetragonal phase of composition close to $UO_{2.43}$ which is apparently related to the fluorite structure. has been described by Grønvold and Haraldsen (78). The density of the phase and the intensities of X-ray reflections point to the substitution of oxide ions for uranium atoms, suggesting the formula $(U_{0.88}O_{0.12})O_2$, a kind of cation deficiency not recognized in other oxide systems. It is possible that the initial absorption of oxygen by UO_2 which occurs without structural or dimensional change may be represented by the introduction of oxide ions into the octahedral cavities among the cations, such as is found in the wide range of the fluorite structure in the system CaF_2–YF_3. Such a proposal has been advanced to explain the fluorite-type structure of the protoactinium oxides $PaO_{2.3}$ and $PaO_{2.5}$ (163). The densities of these phases, however, were not known.

B. MIXED OXIDES OF THE RUTILE TYPE

The rutile structure of titanium dioxide is described on the basis of a tetragonal cell. Somewhat distorted TiO_6 octahedra lie in strings sharing opposite edges along the short *c* axis of the crystal. The unshared oxygen of the octahedra in one string is a "bridge" oxygen of an adjacent string. The structure is shown in Figure 22. The Ti—O—Ti angle is slightly greater than 90° for titanium atoms in the same string and about 120° for titanium in adjacent strings. There is thus some possibility for magnetic interaction. Chromium dioxide, which has this structure, is strongly ferromagnetic.

The mineral rutile frequently contains impurities which are present in the crystal lattice. A sample containing about 28% Nb_2O_5 and 14% Fe_2O_3 was found to have the simple rutile structure (187), and should probably be represented as $(Ti_{0.8}Nb_{0.1}Fe_{0.1})O_2$. In spite of this indication that partial substitution may be effected by valence compensation, such systems have received little attention.

Brandt (22) has shown that stoichiometric phases of composition $A^{3+}B^{5+}O_4$ (A^{3+} = Cr, Fe, Rh when B^{5+} = Nb, Ta; A^{3+} = Al, Cr, Fe, Rh, Ga when B^{5+} = Sb) have the rutile structure with the cations randomly distributed. The compound $RhVO_4$ prepared by heating $[Rh(NH_3)_5Cl]Cl_2$ with vanadium pentoxide in air was also found to have the random rutile structure. It is likely that this compound should be represented as $Rh^{4+}V^{4+}O_4$ in view of the fact that $CrVO_4$ has a different structure which is described as a defect spinal structure having the vanadium atoms in tetrahedral coordination. The chromates $A^{2+}CrO_4$ (A = Ni, Co, Zn, Cd) have similar structures (21).

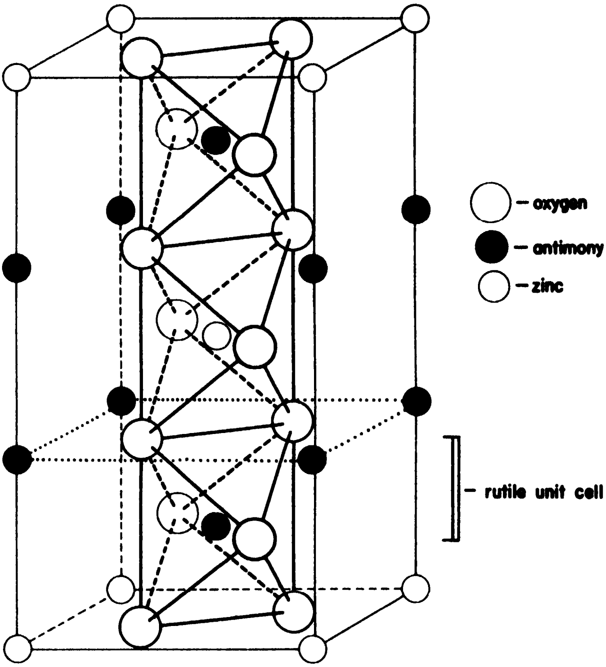


Fig. 22. The trirutile structure of $ZnSb_2O_6$.

When the cations differ in oxidation number by more than 2, they assume an ordered arrangement, and the structure requires a larger unit cell for its description. The trirutile structure shown in Figure 22 represents a common arrangement of cations. It is found in the ternary oxides of pentavalent antimony $M^{2+}Sb_2O_6$ (M = Zn, Mg, Mn, Fe, Co, Ni) (32). The same structure has been assigned to $M^{2+}Ta_2O_6$ (M^{2+} = Mg, Fe, Co, Ni) and to $Fe(Nb,Ta)_2O_6$. The compounds $MnSb_2O_6$, $M^{2+}Ta_2O_6$ (M^{2+} = Zn, Mn), and $M^{2+}Nb_2O_6$ (M^{2+} = Zn, Mg, Fe, Co, Ni) are, however, described by Brandt (22) as having the niobite structure (181). This is an interesting difference between niobium and tantalum if both descriptions are correct.

The niobite structure is described on the basis of hexagonal close packing of oxide ions, the layers being normal to the long axis of the orthorhombic crystal. The metal atoms lie in half the octahedral cavities, forming a kind of layer structure. The sequence of metal ions in the layers is FeNbNb. . . . Edge sharing occurs within these layers with the formation of chains of over-all formulas FeO_4 and NbO_4. It is thus an ordered structure retaining some of the features of the rutile structure.

Another related structure has been found in $NiWO_4$ (99). This compound was originally thought to contain WO_4^{2-} ions, but Keeling has shown that it consists of parallel chains of NiO_6 and WO_6 octahedra. Like octahedra are joined by edges and different octahedra by corners. The structure may therefore be regarded as composed of WO_4 and NiO_4 chains joined together by corner sharing similar in principle to the situation found in the niobite-type compounds. The structure is shown in Figure 23. The metal atoms are displaced from the center of charge of their surrounding oxygen octahedra in a direction parallel to the *b* axis. The two like atoms are equally and oppositely displaced in a manner characteristic of an antiferroelectric substance, but no temperature of transition to a paraelectric material has been found. The displacement would appear to be due to electrostatic repulsion, since the tungsten ions are displaced by 0.3 A., while the nickel atoms are displaced by only 0.13 A. In rutile the oxide ions forming the shared edges of the octahedra are drawn

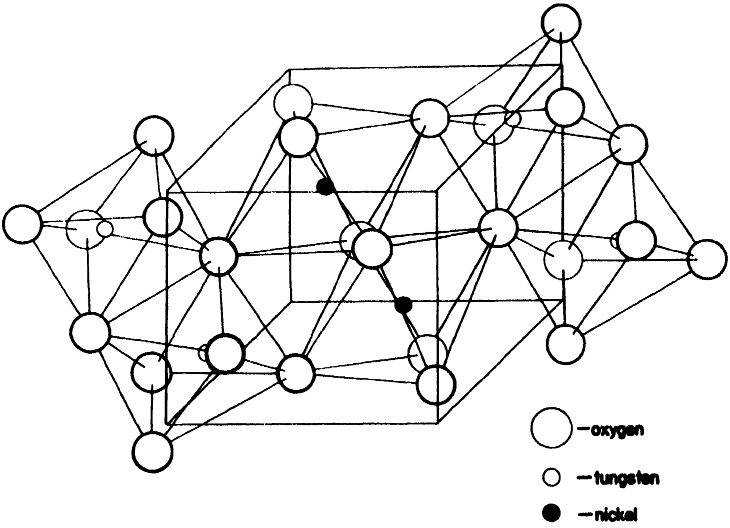


Fig. 23. The structure of $NiWO_4$.

closer together, giving the octahedra an elongated shape in the direction along the *c* axis. This effect has been attributed to cationic repulsion. With the dioxides of molybdenum, tungsten (121), and rhenium (120) a similar kind of edge sharing of MO_6 octahedra is found, but the metal atoms are drawn closer together in alternate pairs of octahedra, which suggests the existence of direct metal–metal bonding. The bond distance decreases with the number of available electrons (119). The mixed oxides TiO_2–VO_2 and VO_2–MoO_2 are also reported to show direct metal–metal interaction (113).

Magneli (113) has observed that there are at least seven distinct phases in the composition range $TiO_{1.75-1.90}$. The experimentally derived compositions of these phases can be expressed by the general formula Ti_nO_{2n-1}, where *n* may have values from 4 to 10 inclusive. The formula Ti_5O_9 was confirmed by single crystal studies. The rutile structure is stable down to the composition $TiO_{1.98}$. The existence of the "homologous" series of phases Ti_nO_{2n-1} is explained by the presence of regularly distributed atomic dislocations in the basic structure of rutile. The dislocations could be anion vacancies similar to those proposed for the CeO_{2-x} phases, but Magneli (122) draws an analogy to the series of phases $(Mo, W)_nO_{3n-1}$ which are derived from the ReO_3 structure. Here the MO_6 octahedra share all corners, each oxygen being in contact with two metal atoms. With decreasing proportions of oxygen, some of the octahedra share edges, and the oxygens involved are in contact with three metal atoms. The structures are described in terms of slabs of MO_3 structure connected to each other by the edge-sharing octahedra. By analogy to this structure, it might be supposed that in the Ti_nO_{2n-1} series, there is a systematic increase in edge-sharing or the introduction of face-sharing between TiO_6 octahedra as *n* decreases.

Anion deficiencies in ternary oxides of this structure containing two different metals do not seem to have been investigated to any extent. A phase of composition $BeOTiO_2$ has been reported to have a rutile-type structure (17), but it seems unlikely that beryllium would be found in octahedral coordination with oxygen. According to Trzebiatowski (193), however, no compound exists in this system, and no change in lattice paramaters of TiO_2 could be detected.

Mixed metal oxides of the rutile type with cation deficiencies have not received much attention. The structure of $V_{12}O_{26}$ is described by Aebi (2) in terms of VO_6 octahedra sharing edges and corners very similar in principle to the intermediate molybdenum oxide Mo_8O_{23}, there being more corner sharing than is found in the rutile structure.

The descriptions of these nonstoichiometric phases appear to suggest some kind of framework structure, but it is difficult to evaluate the difference between increased sharing of oxygen and a simple anion vacancy. Most of the systems for which systematic variation in oxygen sharing is proposed are good semiconductors. Anion vacancy, on the other hand, appears to be the more usual view for insulators, such as are found in systems like CaO–ZrO_2.

C. ABO_4 COMPOUNDS

The transition metals in higher oxidation states tend to yield compounds analogous to those formed by the oxyanions of the nonmetals. The rare earth vanadates, for example, have structures similar to zircon, $ZrSiO_4$. The germanates, $M^{4+}(GeO_4)$, where M^{4+} = Zr, Ce, Th (13), U (46), on the other hand, are isomorphous with scheelite, $CaWO_4$, and only $ThGeO_4$ exists in both forms. Thallium phosphate has been shown to be similar in structure to the chromates M^{2+}-CrO_4 (M^{2+} = Cd, Co, Cu, Ni, V, Zn) (132). Similarities of this kind seem to exist only when the transition metal is in its highest oxidation state. Durif concludes, from consideration of the systematic increase in unit cell dimensions with increase in size of the lanthanide ion, that the cerium vanadium oxide, which was obtained by oxidation of $CeVO_3$, should be written $Ce^{3+}V^{5+}O_4$, a combination of oxidation states, which would not be expected from oxidation potentials. On the basis of either electrode potentials or ionization potentials, one would expect the vanadium chromium oxide to be $Cr^{3+}V^{5+}O_4$ rather than vanadium (II) chromate. These criteria, however, are probably not always applicable to crystals, for the combination of metallic sodium and tungsten(VI) oxide, which is found in the tungsten bronzes, would not be predicted from these considerations. Isomorphous substitution and deviations from stoichiometry have not been extensively investigated in systems of this kind.

A series of compounds MCr_3O_8 (M = an alkali metal) can be made by heating mixtures of the dichromates with chromium trioxide (183). The structure of the potassium compound, as determined by Wilhelmi (209), reveals that two-thirds of the chromium is in tetrahedral coordination and the remainder in octahedral coordination. The CrO_6 octahedra share equatorial oxygens with tetrahedra and are somewhat elongated in that direction, and the CrO_4 tetrahedra have one unshared oxygen, which is much closer to the chromium (~1.53 A.) than the other three (~1.67 A.). The octahedra and tetrahedra form an endless Cr—O layer in the crystal. Molybdenum may be substituted for chromium in the sodium compound up to about $NaMoCr_2O_8$ and vanadium may be introduced in slightly smaller amounts with some change in lattice parameters (20).

The structure of $Li_{1+x}V_3O_8$ has been shown to be different from the chromium compounds (207), although it is also of the layer type. In this case, however, the layers are puckered and are made up of closely coordinated VO_6 octahedra and of VO_5 trigonal bipyramids. Both of these polyhedra are considerably distorted. The lithium ions normally occupy octahedral sites between the layers, but there are also available tetrahedral sites, which may be occupied by additional lithium ions. The electrical properties, the bluish color, and variable cationic content suggest an analogy to the tungsten bronzes. A related sodium compound has a much narrower range of composition, presumably because of the reluctance of sodium ions to occupy a tetrahedral site.

VIII. Conclusion

From the examples of mixed metal oxides which have been discussed, it can be seen that the gross features of the structures of many of these phases have been well established. They are generally described in terms of an "ideal" structure which is based on the concept of closest packing of spherically symmetrical oxide ions. Deviations from the ideal structures are explained on the basis of either unfavorable cationic radii or coulombic repulsion between oxide ions and *d* electrons in orbitals directed toward them or perhaps on the supposition of covalent bond formation. Correlation of these structural deviations and of crystallographic transformations with electronic properties of the crystals has given credence to the interpretations in not a few cases. There remain, however, many systems with properties which are not so readily interpreted. Among these are the phases with substantial cation or anion deficiencies with framework- or layer-type structures.

Perhaps the time is not yet ripe for the development of a comprehensive theoretical treatment of mixed metal oxides. Many of the data relating to their structures and physical properties are tentative, pending the preparation of a suitable specimen. All measurements would be based on single crystals of known composition if they were available. Rarely is this the case.

There is an obvious need to develop methods of synthesis which can be carried out at temperatures low enough to avoid disorder phenomena, departures from stoichiometry, and contamination from containers but under conditions which would favor equilibrium conditions in the crystals. Hydrothermal synthesis, preparations from molten salt solutions, and dry high pressure reactions at moderate temperatures would appear to offer the best opportunity for achieving these conditions.

An intensive and systematic study of these methods is necessary, however, to make them generally applicable to the synthesis of all types of mixed metal oxides.

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